NH-2090

RESEARCH AND DEVELOPMENT OF NEW AND IMPROVED OXIDIZERS FOR USE IN SOLID PROPELLANTS (U)

Final Report
Part I

JANUARY 1963

Prepared for
DEPARTMENT OF THE NAVY
BUREAU OF NAVAL WEAPONS (RMMP-2)
CONTRACT NO. NOrd 18210

Sponsored by
ADVANCED RESEARCH PROJECTS AGENCY
PROPELLANT CHEMISTRY OFFICE
ARPA ORDER NO. 22

ORGANICS DIVISION **Olin**

OLIN MATHIESON CHEMICAL CORPORATION

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FEB 3 1964

OLIN MATHIESON CHEMICAL CORPORATION
ORGANICS DIVISION
NEW HAVEN, CONNECTICUT

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RESEARCH AND DEVELOPMENT OF NEW AND IMPROVED
OXIDIZERS FOR USE IN SOLID PROPELLANTS (U)

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I. INTRODUCTION

This report describes the results of research conducted by Olin Mathieson Chemical Corporation under Contract NOrd 18210 during the period May 15, 1958 - January 14, 1963. This work was monitored initially by the Bureau of Ordnance and, later, by the Bureau of Naval Weapons, Department of the Navy.

At the outset of this work, the specific objective was to develop a fluorine containing solid oxidizer which would deliver a specific impulse of 240 seconds when mixed with conventional fuels in solid propellant formulations. Stability and compatibility requirements were similar to those for ammonium perchlorate. As progress was made in both the fuel and oxidizer areas, the target level of the program was raised to a delivered specific impulse of 280 seconds. For guidance, and assuming an efficiency of 95 %, this corresponds to a calculated theoretical specific impulse of 295 seconds.

During the course of this program, the research areas were limited almost exclusively to compounds containing the elements fluorine, chlorine, nitrogen, oxygen and hydrogen. Carbon containing derivatives were considered to be outside the scope of this program although, occasionally, such derivatives were sought for use as intermediates.

During the course of this research, guidelines for the synthesis effort were supplied by both theoretical performance and thermochemical calculations. Part I of this report describes the laboratory syntheses, experimental results and product evaluation. Part II contains the theoretical performance calculations and describes the methods by which these values were obtained.

II. SUMMARY

A number of tetrafluorochlorate and hexafluorobromate salts were prepared: $CsClF_4$, $RbClF_4$, $KClF_4$, $NOClF_4$, NO_2ClF_4, $CsBrF_6$, $RbBrF_6$, $KBrF_6$, $NaBrF_6$. The more energetic of these ($NOClF_4$ and NO_2ClF_4) were not stable at ambient temperature. Various metathesis type reactions were attempted with these compounds. Evidence for reaction was obtained in a number of cases but unequivocal identification of many of the products could not be made. There are suggestions that the following compounds might have been prepared: ClF_2BF_4, $Al(BrF_6)_3$, and $NO_2BrF_6 \cdot 3-4HF$. Several attempts to confirm the existence of ClF_2BF_4 via metathesis reactions were inconclusive. Positive evidence for a 1:1 adduct, however, was obtained.

The reaction of Cl_2O_7 with N_2F_4 was investigated exhaustively to establish the presence of NF_2ClO_4 in the reaction product. No confirmation of this could be achieved. The major product is $NOClO_4$ plus contaminating metal fluorides. When Cl_2O_7 containing P_2O_5 was used, the compound $NOPF_6$ was produced. This combination of $NOClO_4$ and $NOPF_6$ showed the same $N:F:ClO_4$ ratio as that calculated for NF_2ClO_4. The presence of N-F bonding in the product could not be substantiated.

Corresponding reactions with Cl_2O_6 also were investigated both in the liquid and gas phases. The only products identified were HF complexes of $NOClO_4$ (from the liquid phase) and $NOClO_4$, NO_2ClO_4 and $ClNO_3$ (from the gas phase). Reaction of Cl_2O_6 with HNF_2 produced only $NOClO_4$ and $NOF \cdot 3HF$. When NF_2Cl was used, $NOClO_4$ and $FClO_3$ were formed in addition to some $FClO_2$, $NOCl$ and N_2F_4.

Extensive studies were conducted with the mixed fluorine-chlorine oxides, $FOClO_3$, $FClO_3$ and $FClO_2$. With the perchlorate, in particular, studies were aimed not only at producing new oxidizers but also at achieving some insight into the mode of decomposition of the $FOClO_3$. The $FOClO_3$ was easily prepared and could be handled under ambient conditions with little decomposition. Pertinent results with $FOClO_3$ are:

1. In the gas phase, N_2F_4 is oxidized and only low molecular weight decomposition products are formed.

2. In the liquid phase, or in solvents, N_2F_4 yields $NOClO_4$ and HF complexes of NOF and NO_2F.

3. With NF_2H, extensive and rapid oxidation occurred. In liquid SO_2, the compound NF_2SO_3H was formed.

4. With NF_3 above 150°C., the $FOClO_3$ decomposed to low molecular weight gaseous products and the NF_3 was quantitatively recovered. In an electric discharge, almost complete recovery of the reactants was achieved.

5. With N_2F_2, no products of interest were obtained.

6. With fluorine, some $FClO_3$ was found but its origin could not be established.

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7. No evidence for FO radical formation was found in reactions with $Cl_2C=CF_2$. Halogenated two-carbon and one-carbon derivatives resulted, presumbably by free radical halogenation.

8. With ClF_3, violent decomposition produced low molecular weight gases.

9. With N_2H_4, only hydrazine salts were found and no oxidizing species could be detected.

10. With NH_3, ammonium perchlorate and ammonium fluoride resulted. The formation of $(NH_4)_2SiF_6$ (in glass) also was suspected.

11. No conclusive evidence for a $BF_3 \cdot FOClO_3$ complex could be found. At best, a weak complex may exist at very low temperatures.

In general, experiments with $FClO_3$ showed little reaction. With both BF_3 and NF_3, all reagents were recovered almost quantitatively. The $FClO_3$ proved to be too stable for microwave activation and, in studies with N_2F_4, only decomposition of the N_2F_4 was observed. In an electric discharge the same results were achieved.

With chloryl fluoride, $FClO_2$, no evidence for reaction with NOF or the fluorides of lithium, cesium and magnesium was noted at ambient temperatures or lower. No reactions were conducted at elevated temperatures.

Extensive studies were conducted with N_2F_4 under a variety of activating conditions and with a wide range of reagents. No significant difluoramino derivatives were found although evidence was obtained suggesting the transitory existence of products such as NF_2NO_2 and, possibly, NF_2ClO_3. It was observed that in the range of 2100-2400Å, no decomposition of N_2F_4 occurred, contrary to other reports in the literature. In general, no reaction occurred between N_2F_4 and the perchlorate, chlorate and nitrate salts of lithium and potassium. With $NaClO_2$, extensive decomposition and oxidation were noted when the $NaClO_2$ was moist. When dry, no reaction occurred. Various reactions with $HClO_4$ all failed to show any significant products. It was shown that NOF and NF_2 do not produce NF_3. The reaction of NO_2 with an excess of NF_2 yields only NOF, while the reaction of NF_2 with an excess of NO_2 yields NF_3 and NO.

A number of approaches to new oxidizers was investigated through the reactions of NF_2Cl. In general, it was always possible to isolate the expected by-product but the desired derivative never could be substantiated. For example, with silver salts such as $AgClO_4$ and $AgClO_3$, a quantitative recovery of AgCl usually was obtained but little evidence could be found to indicate the presence of the desired oxidizers.

Interference from glass and metals was noted in many of the reactions of NF_2Cl. This prompted a search for catalytic activity, which was not successful. In most cases where reaction had been observed in glass or metal, it was found not to occur in an all Teflon system. This was particularly

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true with NO_2SbF_6, $NOBF_4$ and NO_2BF_4. Metal definitely catalyzed many of the reactions but complete characterization of the transitory intermediates could not be made. The use of solvents such as nitromethane, chloroform-pyridine and acetonitrile aided reaction but, again, no desirable products could be isolated.

Reactions with NF_2H were generally inconclusive. In most cases, the NF_2H decomposed and the other reactant was recovered almost quantitatively. An attempt to effect 1,4-addition to p-benzoquinone was unsuccessful.

Various reactions of NF_3 were explored. Most of these involved activation of the NF_3. Generally, no reaction, or complete decomposition occurred. No complex formation with either BF_3 or PF_5 could be detected.

The nitridochlorates were investigated as possible routes to oxidizers such as $(NF_2)_2NClO_3$, $(NO)_2NClO_3$, $(ClF_2)_2NClO_3$ and NF_2ClO_3. With K_2NClO_3, no reaction was observed with NF_3 and $FClO_3$. With ClF_3, explosions generally occurred. The existence of $(NO)_2NClO_3$ was suspected but not verified. The new compound Ag_2NClO_3 was prepared. This is a white salt, soluble in mineral acids and ammonia. No suitable solvent could be found in which to conduct subsequent reactions with this new intermediate.

Studies with the barium salts, $Ba(NHClO_3)_2$ and $BaNClO_3$, and with NH_2ClO_3 itself were unfruitful. With the salts, both metathesis reactions and fluorinations were unsuccessful. Attempted fluorinations of solutions of NH_2ClO_3 gave only low molecular weight decomposition products. The only fluorine product of significance was $FClO_3$. Much of this work was complicated by explosions, presumably due to the highly sensitive nature of the reactants.

Several routes to new oxidizers were investigated through the use of the N-fluorocarbamates. The sodium and potassium salts were prepared. The sodium salt is not stable above 0°C. and explodes when warmed. The potassium salt is also unstable, having exploded twice while being handled. An attempt to react the potassium salt with NO_2BF_4 was only partially successful. Although KBF_4 was recovered, only decomposition products of the desired compound could be found. There were indications that $NO_2NFCO_2C_2H_5$ had been prepared but this could not be conclusively established.

Some attempts were made to prepare various oxyfluorochlorates and bromates as intermediates for further use. They did not form by direct reaction of HF with chlorate or bromate salts. No success was achieved in attempting to duplicate the reported preparation of the oxyfluorochlorates of nickel, copper and zinc.

During the course of this research, improved techniques were developed for preparing many of the intermediates among which were NF_2H, NF_2Cl, $FClO_3$ and Cl_2O_6. The thiophenol method gave 70-78% yields of NF_2H from N_2F_4. Fluorine perchlorate was readily prepared by passing fluorine through 70% perchloric acid. The infrared and NMR spectra of $FClO_3$ were recorded and an equation for its vapor pressure developed.

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Dichlorine hexoxide was prepared by treating ClO_2 with ozone. It showed a melting point of +3.5°C. The Cl_2O_6 could be stored for several days in Teflon at -78°C. (shielded from light) with no decomposition.

The corrosive and reactive nature of many of the fluorine compounds required the development of special handling techniques, modified analytical methods, and particularly novel apparatus design before meaningful data could be obtained. These special techniques are described throughout this report.

In the compilation of this report, all of the significant experiments are included even though results in many cases were negative. In some cases only limited data was obtained because of the extreme reactivity of the reagents or the decomposition of unstable products. These experiments, as well as those that did yield new information, are discussed. It is hoped that the extensive results reported here will serve as a guide for future oxidizer research programs.

III. EXPERIMENTAL AND RESULTS

Section I Reactions with Interhalogens

   A. Reactions with ClF₃

Section I Reactions with Interhalogens

  A. Reactions with ClF_3

    1. Objective

The purpose of this study was to prepare new compounds of the type $M^+ClF_4^-$, where M = alkali metal, alkaline earth metal, Al, B, Si, P, or S, or preferably the nitrosyl or nitryl cation, NO^+, and NO_2^+, respectively.

Sharpe and Emeleus (4) had reported the preparation of similar compounds by the solvolysis of alkali metal fluorides with bromine trifluoride, e.g., $KBrF_4$, $AgBrF_4$, and $Ba(BrF_4)_2$. No analogous compounds containing the tetrafluorochlorate ion ClF_4^- had been reported. The preparation of potassium iodohexafluoride, KIF_6, also was described by Emeleus and Sharpe (5).

Several methods were considered for the synthesis of salts containing the chlorotetrafluoride anion. The first method was based on the self-ionization of chlorine trifluoride:

$$2ClF_3 \rightleftharpoons ClF_2^+ + ClF_4^-$$

While the extent of self-ionization in ClF_3 is considerably less than that in both BrF_3 and IF_5 (based on their respective conductivities), some self-ionization could reasonably be expected. If so, then this self-ionization could be shifted to the right by removal of either the ClF_2^+ or the ClF_4^-, as shown.

$$M^+ + F^- + ClF_2^+ + ClF_4^- \rightleftharpoons MClF_4\downarrow + ClF_3$$
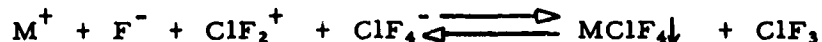
This was indeed the case. Reactions occurred with CsF, RbF, and KF which resulted in the formation of $CsClF_4 \cdot 0.1\,CsF$, $RbClF_4 \cdot 0.2\,RbF$, and $KClF_4 \cdot 0.77\,KF$, respectively. It was not established whether the residual metal fluoride could be removed by refined purification techniques.

A similar reaction occurred with nitrosyl fluoride and ClF_3. The product nitrosyl tetrafluorochlorate, $NOClF_4$, was isolated and characterized.

Attempts to prepare alkaline earth metal tetrafluorochlorates were unsuccessful, apparently due to the lower solubility of these fluorides in chlorine trifluoride. To circumvent this difficulty mixed solvent systems were employed.

In the first method anhydrous hydrogen fluoride was used as an ionizing solvent to bring about the formation of metal tetrafluorochlorates through "neutralization" reactions. This method was based upon the following considerations:

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(a) That the metal fluorides behave as bases in HF, i.e.

$$3HF \rightleftharpoons H_2F^+ + HF_2^-$$

$$MF + HF \rightleftharpoons M^+ + HF_2^-$$
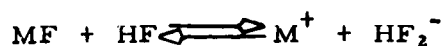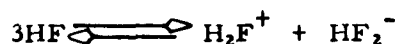
Where M = alkali or alkaline earth metal

(b) That ClF_3 in HF would behave as an acid in the sense that it would compete with proton for a share in the electrons of the fluoride ion, i.e.

$$ClF_3 + 2HF \rightleftharpoons H_2F^+ + ClF_4^-$$
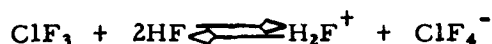
The net result would be a neutralization reaction, which would be expected to occur because of the high dielectric constant of HF and its ability to promote ionization:

$$H_2F^+ + ClF_4^-\ M^+ + HF_2^- \longleftarrow MClF_4 + 3HF$$

There was no experimental evidence that ClF_3 behaves as an acid in HF, although complexes of the type $HF \cdot ClF_3$ had been proposed (1, 2). It has been suggested (3) that ClF_3 behaves as a very strong base in HF, i.e.

$$2HF + ClF_3 \rightleftharpoons ClF_3^{++} + 2HF^-$$
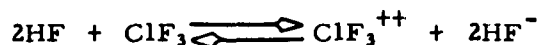
Another route that was employed in the synthesis of various metal tetrafluorochlorates was based on reactions of metal fluorides in mixed solutions of chlorine trifluoride in either bromine pentafluoride or iodine pentafluoride. This study was based on the premise that the solvents might interact in such a way as to alter their normal ionization characteristics. In discussing the equilibria involved when chlorine trifluoride is dissolved in bromine pentafluoride, one should consider:

(1) Self-ionization of the "solvent":

$$2BrF_5 \rightleftharpoons BrF_4^+ + BrF_6^-$$
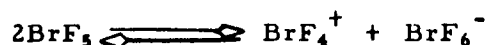
(2) Self-ionization of the "solute":

$$2ClF_3 \rightleftharpoons ClF_2^+ + ClF_4^-$$

(3) Assuming the ionization of the solute as an "acid" in the solvent, the following equilibrium would be established:

$$ClF_3 + BrF_5 \rightleftharpoons BrF_4^+ + ClF_4^-$$
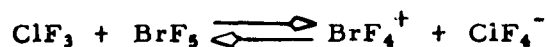
Since the bromine pentafluoride is also acting as the solvent for the metal fluoride (base), the following solvolytic reaction would also

take place:

$$MF + BrF_5 \rightleftharpoons M^+ + BrF_6^-$$

$$(M^+) + (BrF_6^-) + (BrF_4^+) + (ClF_4^-) \rightleftharpoons MClF_4 + 2BrF_5$$
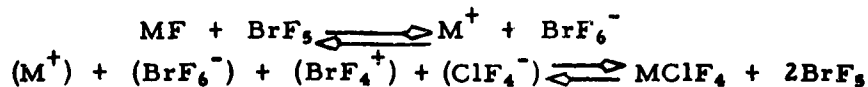
In this manner possible increase of the extent of ionization of chlorine trifluoride would occur, thus increasing the probability of forming $MClF_4$ type compounds over what could be formed by simple solvolysis:

$$MF + ClF_3 \rightleftharpoons M^+ + ClF_4^-$$
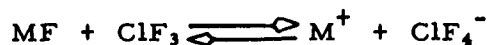
If the solute, chlorine trifluoride, were to ionize as a base in liquid bromine pentafluoride, the reaction would be:

$$ClF_3 + BrF_5 \rightleftharpoons ClF_2^+ + BrF_6^-$$

with the result that the concentration of BrF_6^- ions in the solution would be increased. This would result in a greater probability of formation of $MBrF_6$ type compounds, as would be expected from the Law of Mass Action.

The above argument also holds for the system: chlorine trifluoride-iodine pentafluoride-metal fluoride, where ClF_3 is taken to be the "solute" and IF_5 the "solvent".

Experimental evidence indicates, however, that in the mixtures ClF_3-BrF_5, and ClF_3-IF_5, chlorine trifluoride is acting as a base, with the second component of the solution donating the complex anion. Thus, in the ClF_3-BrF_5-MF system:

$$ClF_3 + BrF_5 \rightleftharpoons ClF_2^+ + BrF_6^-$$

$$MF + ClF_2^+ + BrF_6^- \rightleftharpoons MBrF_6 + ClF_3;$$
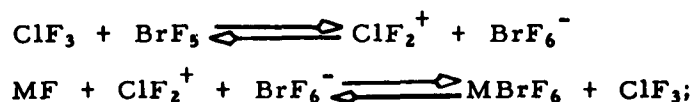
and for the ClF_3-IF_5-MF system:
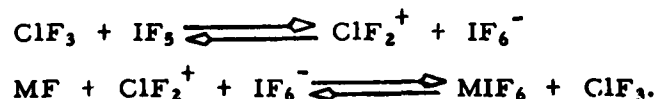
$$ClF_3 + IF_5 \rightleftharpoons ClF_2^+ + IF_6^-$$

$$MF + ClF_2^+ + IF_6^- \rightleftharpoons MIF_6 + ClF_3.$$

Experimental evidence for the above series of reactions was indicated in the interaction of potassium fluoride with chlorine trifluoride in iodine pentafluoride. This led to the formation of potassium iodohexafluoride, KIF_6, first reported by Emeleus and Sharpe (5). These solvent systems did not yield the desired tetrafluorochlorate salts. The most notable success was achieved with chlorine trifluoride alone.

The ClF_3 used was 99.0% pure, from the Matheson Company, Inc. Prior to use, it was passed over NaF pellets maintained at 100°C. in a Monel tube to remove HF impurities.

2. Reactions with Group I Metal Fluorides

a. ClF_3 + LiF

Material

LiF. American Potash and Chemical Corporation. The LiF was dried by heating under vacuum at 110-120°C. for 16 hours.

Apparatus

The general purpose vacuum lines constructed for this work are shown in Figure 1. The vacuum equipment was constructed of Pyrex and metal, joined by means of a copper to Pyrex No. 774 (Housekeeper) seal. The Pyrex portion of the apparatus consisted of the nitrogen gas inlet and drying column, a mercury pressure release vent, a three-way Pyrex stopcock and a trap immersed in liquid nitrogen which served to protect the mercury manometer and the Duo-Seal vacuum pump.

The remainder of the apparatus was constructed of 1/4 inch O.D. copper tubing, with brass fittings and miniature forged Monel needle valves with Teflon packing. The traps were constructed from Monel pipe with silver soldered copper tubing inlets and outlets. Each vacuum line was also equipped with a pressure gauge which operated in the range 30 inches vacuum to 30 psi pressure.

The HF absorber was constructed of Monel pipe. The Monel pipe was placed inside a Fisher hinged multiple unit combustion furnace in which the temperature was controlled by means of a Brown-Pyr-O-Vane (Minneapolis Honeywell Company) controller.

The apparatus was rigorously cleaned and dried before assembly and a thin layer of Teflon "T-Film" (Eco Engineering Company) thread compound was used on all pipe connections.

Reactions were conducted in round-bottom Pyrex or Vycor flasks which were attached to the metal line by means of standard taper joints, a 2 mm. stopcock and a copper to Pyrex glass No. 774 (Housekeeper) seal as in nickel reactors. The nickel reactors were fitted with Monel needle valves and brass connections for the low pressure reactions. In the study of the reactions between alkali metal fluorides and chlorine trifluoride at 100°C., modified nickel reactors were wrapped with heating tape and asbestos. Temperature control was maintained by means of a Brown-Pyr-O-Vane temperature regulator (Minneapolis Honeywell Corporation).

The apparatus is shown in Figure 2.

Procedure

In experiments using liquid hydrogen fluoride as the solvent, the metal fluoride was placed in the nickel reaction vessel which was, in turn, connected through a Hoke Monel needle valve to the metal vacuum line.

Figure 1

General Purpose Apparatus for the Synthesis of Interhalide Complexes
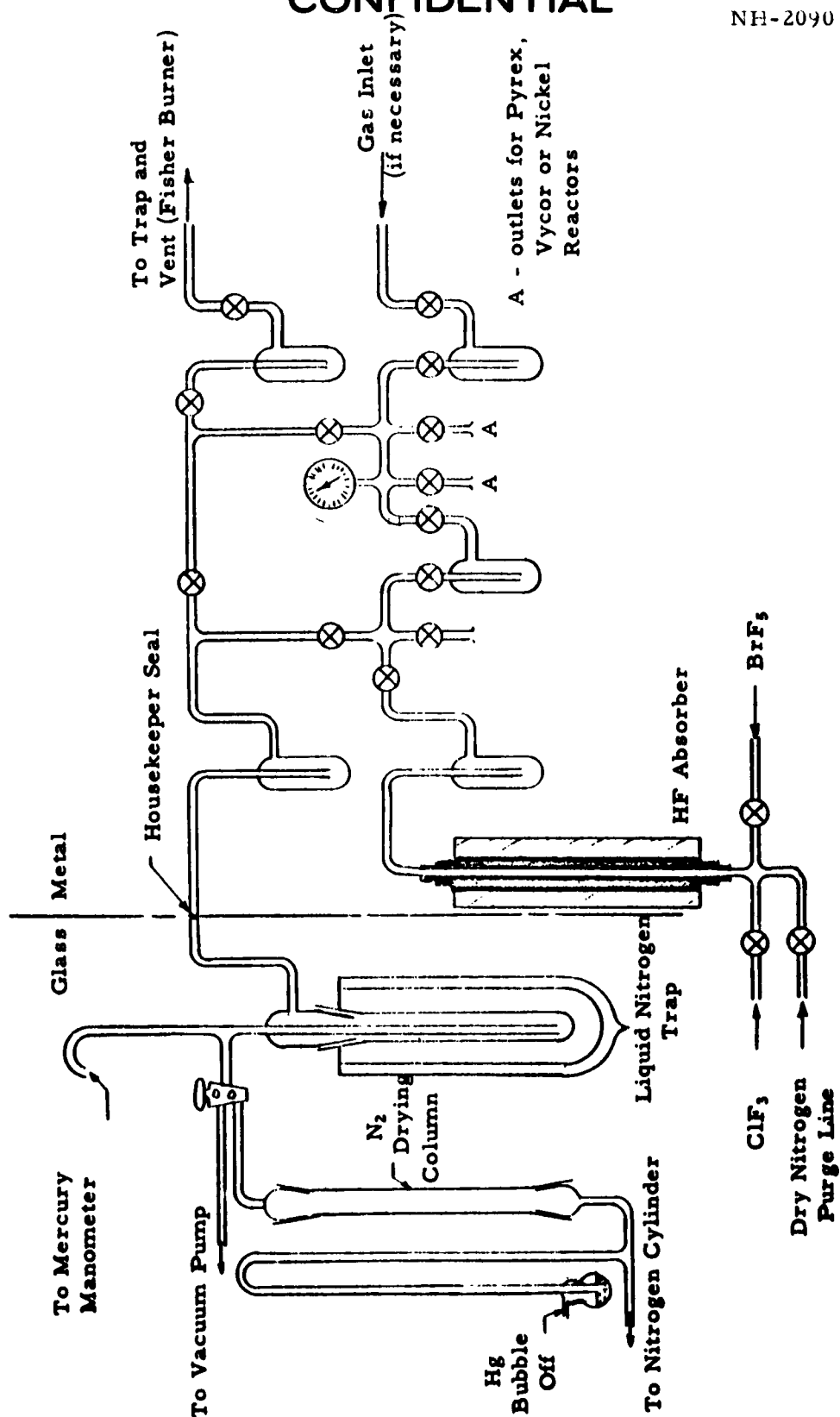
After evacuation of the system, anhydrous hydrogen fluoride was distilled into the reaction vessel from the supply cylinder by placing the reaction vessel in a -78°C. bath (trichloroethylene-Dry Ice). It was found that a sufficient quantity of anhydrous HF was easily transferred in 10 to 20 minutes.

Chlorine trifluoride was allowed to distill directly from the supply cylinder into a calibrated Pyrex tube, whch was cooled to -196°C., by means of standard taper joints and a metal to Pyrex glass No. 774 (Housekeeper) seal. For lubrication of the Pyrex standard taper joints, Kel-F grease (The M. W. Kellogg Company) was found to be satisfactory.

It was found that ClF_3, when free of HF, can be handled in Pyrex without etching taking place. After the required amount of ClF_3 had been condensed in the calibrated tube, the liquid nitrogen bath was replaced by a trichloroethylene-Dry Ice bath followed by an ice bath to allow elemental chlorine and/or chlorine monofluoride impurities to vaporize. During this operation the system was constantly purged with dry nitrogen which carried the impurities, along with a small amount of chlorine trifluoride, to the vent. After the system was thoroughly flushed with nitrogen the ice bath was replaced by a liquid nitrogen bath and the entire system once again evacuated. The ClF_3 was then distilled into the anhydrous HF solution at room temperature by placing a -78°C. bath around the nickel reactor. The quantity of ClF_3 added was readily determined from the volume of liquid in the calibrated tube and the density of ClF_3 at 0°C.

After the solution was allowed to stand (with occasional shaking) for a predetermined length of time, the reaction vessel was returned to the vacuum line, the volatile components distilled off and the reaction product pumped on until a constant weight was obtained. All of these operations were performed at room temperature.

In the study of the alkali metal fluorides-chlorine trifluoride or bromine pentafluoride systems, the procedure followed was generally the same with the exception that in some cases Pyrex or Vycor reactors were employed and, of course, no HF was added to the reactors. The procedure for handling BrF_5 in the vacuum system was identical to that outlined for ClF_3.

In performing these experiments, the required amount of metal fluoride was transferred to the reactor, the reactor attached to the vacuum line and the reactor was returned to the line, the unreacted ClF_3 or BrF_5 removed by distillation at room temperature and the product pumped on until a constant weight was obtained. Final opening of the bomb and removal of the product was performed in a dry box under a nitrogen atmosphere.

Results

This reaction was expected to occur as follows:

$$2ClF_3 \rightleftharpoons ClF_2^+ + ClF_4^-$$

$$LiF + ClF_3 \rightleftharpoons Li^+ + ClF_4^-$$

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Figure 2

Apparatus for the Reaction Between Alkali Metal Fluorides
and Chlorine Trifluoride at 100° C.

0-600 PSIG ASHCROFT GAUGE

MONEL NEEDLE VALVE

NICKEL BOMB

ARM OF BURRELL SHAKER

BRISKEAT HEATING TAPE

ASBESTOS

THERMOCOUPLE

HEATER LEADS

(TO PYR-O-VANE CONTROLLER)

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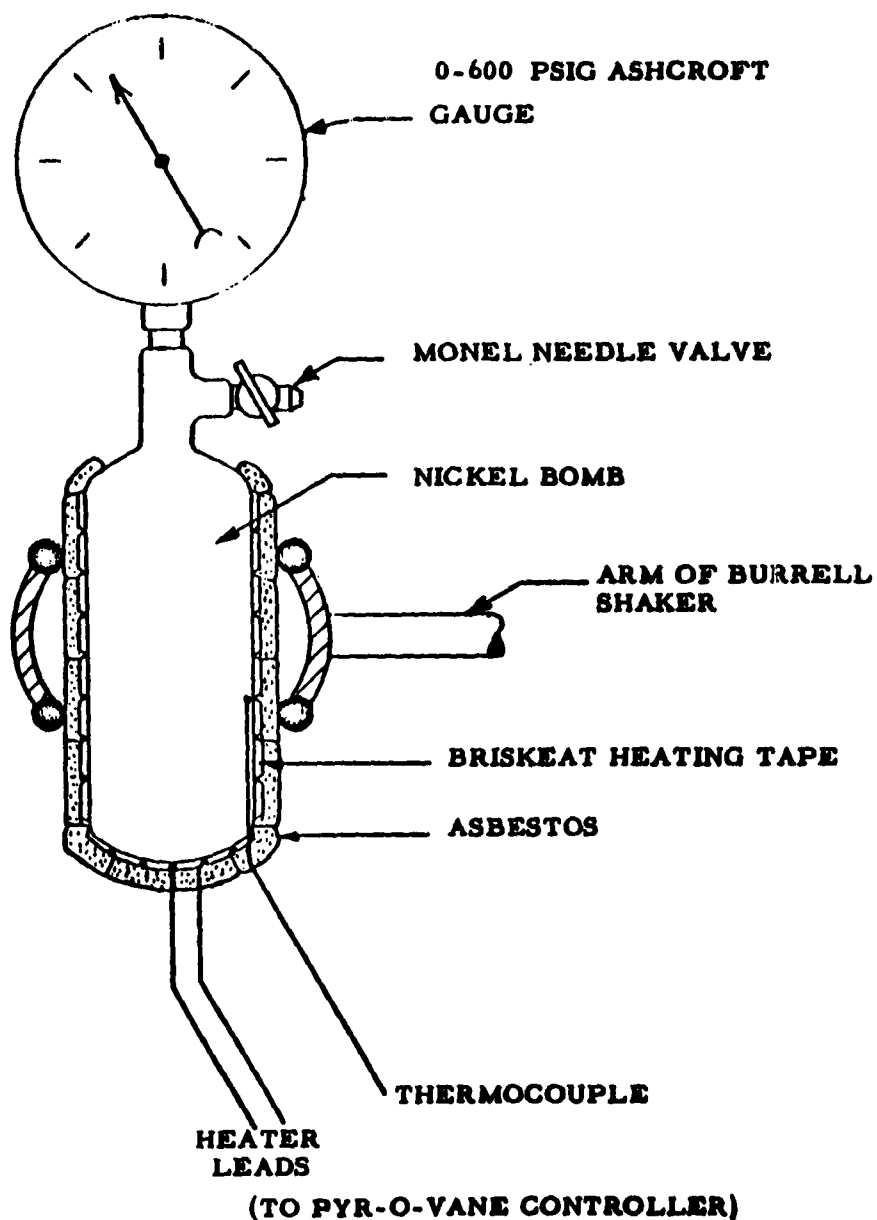
At 0°C. there was no appreciable solvolysis of LiF in ClF$_3$ and the expected product, Li$^+$ClF$_4^-$, was not obtained. The reactants were recovered and unchanged.

b. ClF$_3$ + NaF

Material

NaF. The Matheson Company, Matheson, Coleman, and Bell Division, A.C.S. Reagent Grade. The NaF was dried by heating under vacuum at 110-120°C. for 16 hours.

Apparatus and Procedure

The apparatus and procedure are described in 1A, 2a.

Results

In chlorine trifluoride, the following reaction was expected to occur:

$$2ClF_3 \rightleftharpoons ClF_2^+ + ClF_4^-$$
$$NaF + ClF_3 \longrightarrow Na^+ + ClF_4^-$$
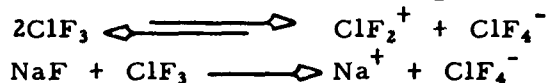
At 0°C. there was no appreciable solvolysis of NaF in ClF$_3$. The expected product Na$^+$ClF$_4^-$ was not formed. The reactants were recovered unchanged.

c. ClF$_3$ + KF

Material

KF. General Chemical Division, Allied Chemical and Dye Corporation, Reagent Grade. The KF was dried before use by heating under vacuum at 110-120°C. for 16 hours.

FC-75. Minnesota Mining and Manufacturing Co., used as received(6).

Apparatus and Procedure

Same as described in 1A, 2a.

Results

The solvolysis reaction between KF and ClF$_3$ at 100°C. led to the formation of a solid product. Apparently the following reaction occurred:

$$KF + 2ClF_3 \xrightarrow[\text{16 hrs.}]{100°C.} K^+ClF_4^- + ClF_3$$
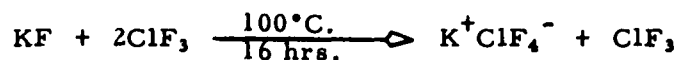
The experimental conditions are listed in Table 1. Based upon weight of reacted KF, a 56.5% conversion of KF to KClF$_4$ had occurred, giving a material with the composition KClF$_4$·0.77KF. Analysis showed:

		Found	Theoretical for KClF$_4$·0.77KF
Wt. %	Cl	14.7 ± 0.2	18.2
	F	46.7 ± 0.1	46.5

The chlorine analysis is questionable.

The thermal decomposition of KClF$_4$·0.77KF was measured. The apparatus is described in Figure 3. Slow decomposition was apparently taking place at 200°C. since at this temperature the sample had decreased in weight by approximately 4%. At 300°C.,91.5% of the sample (based upon the weight of the original KClF$_4$ content) had decomposed. The decomposition products were not identified.

Table 1

Solvolysis Reactions Between Alkali Metal Fluorides and Chlorine Trifluoride

Experiment No.	Quantity of ClF₃ grams	moles	Metal Fluoride (MF)	Quantity of MF grams	moles	Mole Ratio MF	ClF₃	Reactor	Reaction Temp. (°C)
1807D-44	49.2	0.533	CsF	9.992	0.070	1	7.6	Nickel	100
1807D-47	51.4	0.556	RbF	8.067	0.077	1	7.2	Nickel	100
1807D-30	54.5	0.591	KF	4.322	0.074	1	8.0	Nickel	100

Experiment No.	Contact Time (hours)	Weight of Product (grams)	Analysis (%) Cl	F	Remarks
1807D-44	16	15.92	14.4±0.1	30.8±0.1	Based upon weight of product, a 91.0% conversion of CsF to CsClF₄ had occurred, giving a material with the composition: CsClF₄·0.10 CsF (I). Theoretical for (I): Cl=13.7% F=30.0%.
1807D-47	16	14.14	15.4±0.3	37.3±0.0	Based upon weight of product, an 85.2% conversion of RbF to RbClF₄ had occurred giving a material with the composition: RbClF₄·0.18 RbF (II). Theoretical for: (II); Cl=16.5%; F=36.9%.
1807D-30	48	8.303	14.7±0.2	46.7±0.1	Based upon weight of product, a 56.5% conversion of KF to KClF₄ had occurred, giving a material with the composition KClF₄·0.77KF (III). Theoretical for (III): Cl=18.2%; F=46.5%

The density of $KClF \cdot 0.77\ KF$ was determined by the displacement method employing 5- and 10-mL pycnometers, and Fluorochemical FC-75 as the displaced liquid. Fortunately, the salt did not react with the fluorocarbon and it was not soluble. The results are listed in Table 2. The density is 2.58 ± 0.10 g./ml. at 23.0 - 24.5°C.

d. $ClF_3 + RbF$

Material

RbF, American Potash and Chemical Corporation. The salt was dried before use by heating under vacuum at 110-120°C. for 16 hours.

Apparatus

The apparatus is described in Figures 1 and 2 and in 1A, 2a.

Procedure

The procedure is described in 1A, 2a.

Results

The solvolysis reaction between RbF and ClF_3 at 100°C. led to the formation of a light pink solid product. Apparently the following reaction occurred:

$$RbF + 2ClF_3 \xrightarrow[\text{16 hrs.}]{100°C.} Rb^+ClF_4^- + ClF_3$$
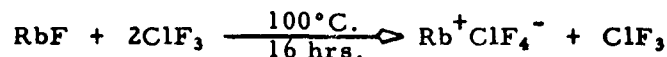
The experimental conditions are listed in Table 1. The conversion of RbF to $RbClF_4$ was 85.2%. As in the case of $KClF_4$, all of the metal fluoride could not be removed. The isolated solid had the composition $RbClF_4 \cdot 0.18RbF$. This is a calculated composition based on weight gain of reacted RbF. Actual elemental analysis showed:

	Found	Theoretical $RbClF_4 \cdot 0.18RbF$
Wt. % Cl	15.4 ± 0.3	16.5
% F	37.3 ± 0.0	36.9

e. $ClF_3 + CsF$

Material

CsF. American Potash and Chemical Corp. The CsF was dried by heating under vacuum at 110-120°C. for 16 hours. Emission spectrographic analysis indicated that this material contained 0.005 to 0.05% silicon.

Apparatus

The apparatus is described in 1A, 2a and in Figures 1 and 2.

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Table 2

Densities of Solid Potassium and Cesium Tetrafluochlorides at 23.0 - 24.5°C.

Experiment No.	Material	Density (g/ml)			Average Density (g/ml)
		I	II	III	
1807D-60	CsClF$_4 \cdot$ 0.1CsF	3.371	3.432	-	3.40 $\pm$ 0.03
1807D-62	KClF$_4 \cdot$ 0.77KF	2.563	2.736	2.458	2.58 $\pm$ 0.10

Procedure

The procedure is described in 1A, 2a.

Results

The solvolysis reaction between CsF and ClF_3 at 100°C. resulted in the formation of a light pink solid.

$$CsF + 2ClF_3 \xrightarrow[\text{16 hrs.}]{100°C.} Cs^+ ClF_4^- + ClF_3$$
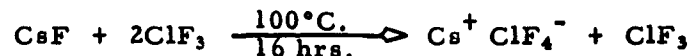
Experimental conditions are listed in Table. 1. The conversion of CsF to $CsClF_4$ was 91.0%. As in the cases of $KClF_4$ and $RbClF_4$, the product was not isolated as pure $CsClF_4$. The composition of the solid based on weight gain of reacted CsF was $CsClF_4 \cdot 0.10CsF$. The actual elemental analysis was:

		Found	Theoretical for $CsClF_4O \cdot 0.10CsF$
Wt. %	Cl	14.4±0.1	13.7
	F	30.8±0.1	30.0

The effects of thermal treatment of $CsClF_4 \cdot 0.10CsF$ are shown in Table 3. The $CsClF_4$ was found to be unusually stable (300°C.) as compared to the alkali metal polyhalide compounds in general. It may be hypothesized that the compound $CsClF_4$ has a high percentage of ionic character in the metal-halide bonds. This may be due in part to

(a) the relatively low ionization potential of cesium as compared to the other members of the alkali series, and

(b) to the highly electronegative nature of the ClF_4^- anionic group.

Table 1 shows that the relative extent of conversion of alkali metal fluoride to polyhalides in the chlorine trifluoride system is in the same order as in the bromine pentafluoride system

$$CsF > RbF > KF$$

It is interesting to note that both the cesium product ($CsClF_4 \cdot 0.1CsF$), and the rubidium product ($RbClF_4 \cdot 0.2RbF$) were light pink in color. Considering the polarizability of ions, the greater the number of additional electrons there are present the less strongly is the electron cloud bound to the nuclei and the greater its deformation by the field. Polarizability is much greater with anions than with cations, for with cations the positive charge will tend to counteract the displacement of the electrons by the applied field (7). Cesium and rubidium ions have the highest polarizability in the alkali metal series. In the compounds $CsClF_4$ and $RbClF_4$, both cation and anion have relatively high polarizabilities with the result that electron excitation in these compounds may be possible with visible light. The pink color of these salts may indeed be taken as an indication of their deviation from pure ionic bond character (8).

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Table 3

Central Analysis of Cesium Tetrafluochloride

$(CsClF_4 \cdot 0.1CsF)$ After Thermal Treatment

Material	Chlorine (%)	Fluorine (%)
Theoretical for $CsClF_4 \cdot 0.1CsF$	13.7	30.0
Salt prepared in experiment 1807D-44	14.4 $\pm$ 0.1	30.8 $\pm$ 0.1
Salt prepared in experiment 1807D-44 after heating to 300° for 4 - 6 hours.	13.9 $\pm$ 0.1	29.7 $\pm$ 0.1

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Compound vacuum-pressure gauge -30 in. of mercury to +30 p.s.i.g.

Copper vacuum line

Monel needle valve

Glass-copper housekeeper seal

Thermometer

Std. taper Pyrex joint

Stopcock

Paddle stirrer

Pyrex reactor

Knife-edge heater

Dewer flask
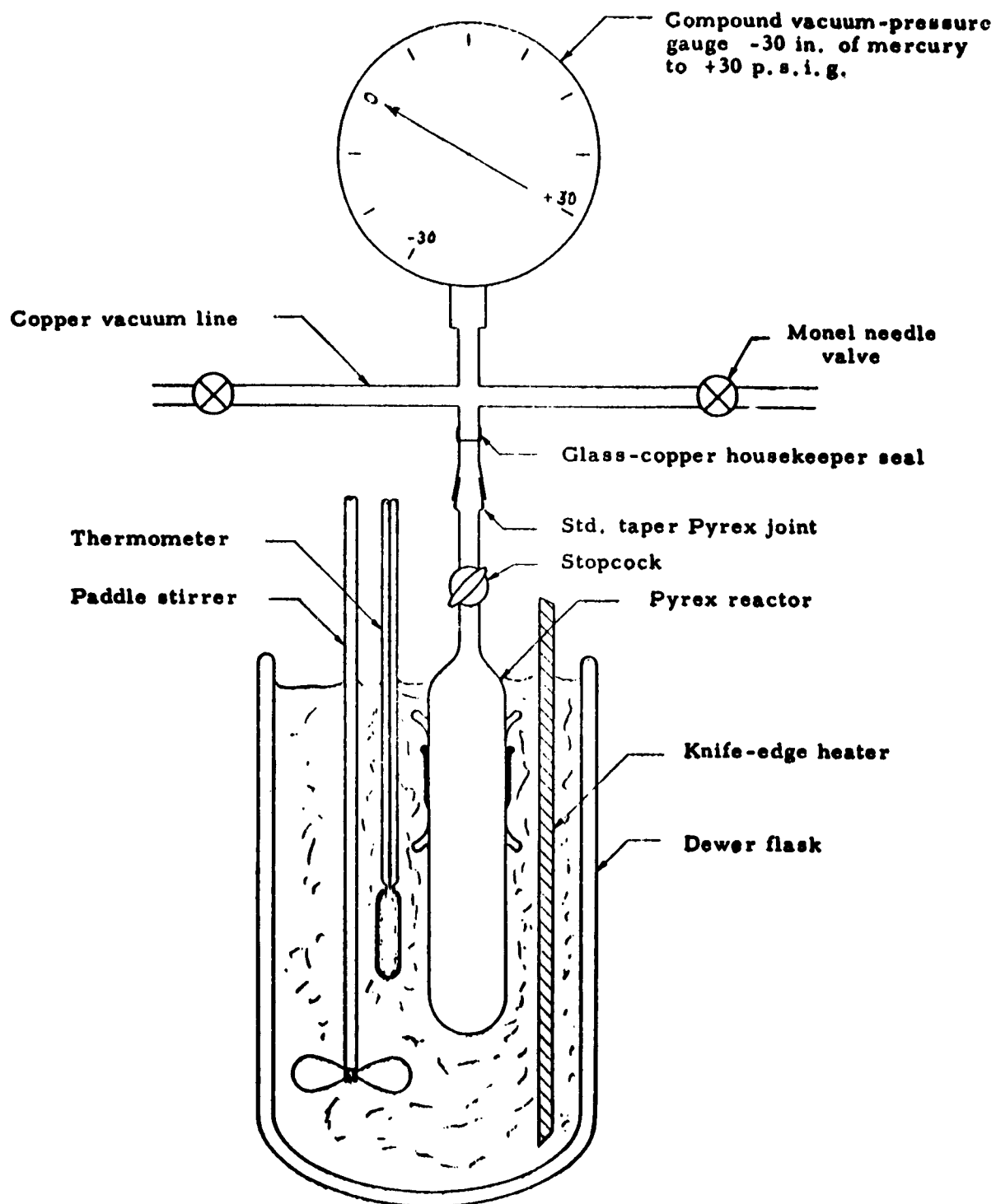
The density of $CsClF \cdot 0.1CsF$ was determined by the displacement method, employing 5- and 10-ml. pycnometers, and Fluorochemical FC-75. The results are listed in Table 2. The density of $CsClF_4 \cdot 0.1CsF$ at 23.0-24.5°C. is 3.40 ± 0.03 g./ml.

f. ClF_3 + Metal Fluorides in HF

Material

LiF. American Potash and Chemical Corp.

CsF. American Potash and Chemical Corp.

KF. Allied Chemical and Dye Corp., General Chemical Div.

NaF. The Matheson Co., Inc., Matheson, Coleman and Bell Div.

The metal fluorides were dried by heating under vacuum at 110-120°C. for 16 hours.

HF. The Matheson Co., Inc. Anhydrous. Purity 99.0%.

Apparatus

The apparatus is described in 1A, 2a and Figures 1 and 2.

Procedure

The procedure is described in 1A, 2a.

Results

In these investigations anhydrous HF was employed as an ionizing solvent to bring about the formation of metal tetrafluorochlorates through "neutralization" reactions as shown.

$$3HF \rightleftharpoons H_2F^+ + HF_2^-$$

$$MF + HF \rightleftharpoons M^+ + HF_2^-$$

$$ClF_3 + 2HF \rightleftharpoons H_2F^+ + ClF_4^-$$
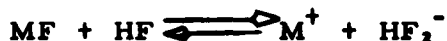
where $M = Li^+$, Na^+, K^+, and Cs^+

The net result would be a neutralization reaction which was expected to occur because of the high dielectric constant of HF and its ability to promote ionization

$$H_2F^+ + ClF_4^- + M^+ + HF_2^- \longrightarrow MClF_4 + 3HF$$

In these experiments the reactants ClF_3, HF and the metal fluoride were placed in a nickel vessel and permitted to stand for several hours at

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room temperature. The mole fraction of the metal fluoride in the HF was sufficient to assume complete solution of the metal fluoride.

There was no evidence for the formation of the corresponding metal tetrafluorochlorates. From the data obtained in this work, the behavior of ClF_3 was not determined since, in HF, the relatively more stable metal bifluorides (MHF_2) were formed. It is interesting to note that with LiF and NaF pure $LiHF_2$ and $NaHF_2$, respectively, were easily obtained, whereas for fluorides containing larger cations i.e., KF and CsF, the pure bifluorides could not be obtained in an equivalent time.

The analytical method used for determining the amount of HF in the products was checked against a chemically pure sample of the metal bifluoride. In the case of $NaHF_2$ analysis showed:

	Found	Theoretical $NaHF_2$
Wt. % HF	32.4 ± 0.2	32.3

The degree of coordination and/or solvation of the various fluorides as deduced from this work is in logical agreement with the extent of solution of the corresponding metal fluorides in anhydrous HF, i.e.,

$$CsF > RbF > KF > NaF > LiF$$

The attempted synthesis of alkali metal tetrafluorochlorates at room temperature in anhydrous hydrogen fluoride as the solvent was not successful. This may be due to the fact that chlorine trifluoride does not ionize as an acid in HF, or, more probably, that due to the greater stability of the HF_2^- ion, only the corresponding bifluorides were obtained.

g. ClF_3 and Metal Fluorides in BrF_5

Material

KF. Allied Chemical and Dye Corp., General Chemical Division, Reagent Grade.

NaF. The Matheson Co., Matheson, Coleman and Bell Division.

The metal fluorides were dried before use by heating under vacuum at 110-120°C. for 16 hours.

BrF_5. Allied Chemical and Dye Corp., General Chemical Division.

The BrF_5 was purified before use by passing the vapors through a Monel tube containing NaF pellets at 100°C. to remove traces of HF and BrF_3 and then vacuum fractionated to remove F_2.

Apparatus

The apparatus is described in 1A, 2a and Figures 1 and 2.

Procedure

The procedure is described in 1A, 2a. The reactants BrF_5 and ClF_3 and the metal fluoride were placed in the nickel reactor and allowed to stand at 100°C. for approximately 70 hours. The products were then fractionated.

This study, as described earlier, was based on the premise that the solvents ClF_3 and BrF_5 might interact in such a way as to alter their normal ionization characteristics. If the solute, ClF_3, were to ionize as a base in liquid BrF_5, the reaction would be:

$$ClF_3 + BrF_5 \rightleftharpoons ClF_2^+ + BrF_5^-$$

If, as an acid,

$$ClF_3 + BrF_5 \rightleftharpoons BrF_4^+ + ClF_4^-$$

Results are listed in Table 4. There is no evidence suggesting the formation of $MBrF_6$. Instead, only $KClF_4$ was formed, thus suggesting that ClF_3 ionizes as an "acid" in BrF_5.

$$ClF_3 + KF \xrightarrow[\substack{100°C. \\ 72 \text{ hrs.}}]{BrF_5} KClF_4$$
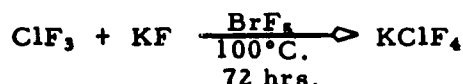
The conversion of KF to $KClF_4$ was 59.4%. Based on the weight gain of the reacted KF, the product composition was calculated as $KClF_4 \cdot 0.69$ KF.

		Found	Theoretical for $KClF_4 \cdot 0.69$ KF
Wt%	Cl	15.8±0.5	18.6
	F	46.4±0.1	46.7
	Br	2.5±0.2	0.0

The yield of solid and the product composition from reactions utilizing BrF_5 as the solvent were essentially the same as those from reaction of ClF_3 and KF alone.

	With BrF_5	No BrF_5
Conversion of KF	59.4%	56.5
Product composition	$KClF_4 \cdot 0.77$KF	$KClF_4 \cdot 0.69$KF

The solvent effect of BrF_5 on the reaction of ClF_3 with NaF was also investigated. The expected analogous reaction:

$$NaF + ClF_3 \xrightarrow[\substack{100°C. \\ 68 \text{ hrs.}}]{BrF_5} NaClF_4$$
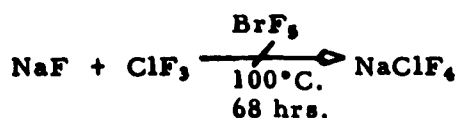
Table 4

Solvolysis of Alkali Metal Fluorides In Mixed Halogen Fluorides

Exp. No.	Quantity of ClF₃ grams	moles	Quantity of BrF₅ grams	moles	Metal Fluoride (MF)	Quantity of MF grams	moles	Mole Ratio MF	ClF₃	BrF₅	Reactor
1807D-33	58.5	0.634	115.7	0.661	KF	3.236	0.056	1	11.4	11.9	Nickel
1807D-42	37.4	0.405	90.6	0.518	NaF	2.991	0.071	1	5.7	7.3	Nickel

Exp. No.	Reaction Temp. (°C.)	Contact Time (hours)	Weight of Product (grams)	Analyses (%) Cl	F	Br
1807D-33	100	72	6.283	15.8±0.5	46.4±0.1	2.5±0.2
1807D-42	100	68	3.595	-	-	-

Remarks

1807D-33   Based upon weight of product, a 59.4% conversion of KF to KClF₄ had occurred, giving a material with the composition: KClF₄ · 0.69 KF (I). Theoretical for (I): Cl=18.6%; F=46.7%.

1807D-42   No analyses obtained since quantity of halogen fluorides retained was small.

did not occur. As noted previously, a reaction did not occur with NaF and ClF$_3$. The reactants were recovered.

h. ClF$_3$ and Metal Fluorides in IF$_5$

Material

IF$_5$. Allied Chemical and Dye Corp., General Chemical Division. The IF$_5$ was purified by vacuum fractionation.

CsF. American Potash and Chemical Corporation

LiF. American Potash and Chemical Corporation

KF. Allied Chemical and Dye Corporation, General Chemical Division, Reagent Grade.

RbF. American Potash and Chemical Corporation

NaF. The Matheson Co., Inc., Matheson, Coleman, and Bell Division, A.C.S. Reagent Grade.

The alkali metal fluorides were dried before use by heating under vacuum at 110-120°C. for 16 hours.

Apparatus

The apparatus is described in 1A, 2a and in Figures 1 and 2.

Procedure

The general procedure is described in 1A, 2a.

Results

Experimental evidence indicates that in the solvent mixture ClF$_3$-IF$_5$ chlorine trifluoride is acting as a "base", with the second component of the solution donating the complex anion. Thus in the ClF$_3$-IF$_5$ -MF system:

$$ClF_3 + IF_5 \rightleftharpoons ClF_2^+ + IF_6^-$$

$$MF + ClF_2^+ + IF_6^- \rightleftharpoons MIF_6 + ClF_3$$
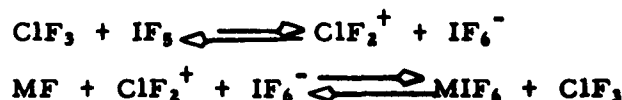
M = alkali metal

Experimental evidence for the above series of reactions was indicated in the interaction between KF and the solvent system ClF$_3$ in IF$_5$. This reaction led to the formation of potassium iodohexafluoride (KIF$_6$), first reported by Emeleus and Sharpe (5). Indirect proof that this compound was prepared was based upon the weight per cent iodine in the product and the measured "oxidizing power". The oxidizing

power was measured as equivalents of iodine per gram of sample and is based upon the following reactions:

$$KIF_6 + 3H_2O \longrightarrow KIO_3 + 6HF$$

$$KIO_3 + 5KI + 6HCl \longrightarrow KCl + 3H_2O + 3I_2$$

The reactions with LiF, NaF, CsF, and RbF resulted in complex products which could not be readily fractionated in this preliminary investigation. The only identified product obtained from this study was KIF_6, a white solid.

3. Reaction With Group II Metal Halides

a. $ClF_3 + MgF_2$

Material

MgF_2. The Matheson Co., Inc., Matheson, Coleman and Bell Division, Reagent Grade.

Apparatus

The general purpose metal high vacuum equipment and metal reactors are described in Figures 1 and 2 and in section 1A, 2a.

Procedure

The general technique for handling halogen fluorides as performed in solvolysis reactions leading to the formation of polyhalide salts is described in section 1A, 2a.

Results

Magnesium fluoride and excess chlorine trifluoride were placed in a nickel reactor, Figure 2. The reactor was then placed in a rocking device for 16 hours at 100°C. The expected reaction was:

$$MgF_2 + 2ClF_3 \longrightarrow\!\!\!\!\!\!/\!\!\!\!\longrightarrow Mg(ClF_4)_2$$
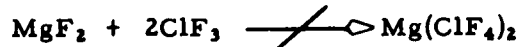
Sharpe and Emeleus (4) had prepared the polyhalide salt $Ba(BrF_4)_2$ by treating a barium halide with BrF_3. Since bromine trifluoride is a good ionizing solvent (9), this observation substantiates the conclusion that the criterion for extensive solvolysis of a metal compound in a halogen fluoride is that either a volatile or reagent-soluble fluoride be formed(10). It would appear, therefore, that, in general, solvolysis reactions involving alkaline earth metal fluorides should proceed with more difficulty than the corresponding reactions with alkali metal fluorides. For example, in anhydrous HF, the alkaline earth fluorides are all less soluble than the alkali metal fluorides (except for SrF_2 as compared to LiF) (11). Where data are available, the above observations also appear to apply to the solubility of alkali and alkaline

earth fluorides in bromine trifluoride (12).

b. $ClF_3 + MgCl_2$

Material

MgCl$_2$. J. T. Baker Chemical Co., Reagent Grade.

Apparatus

The general purpose metal high vacuum equipment and metal reactor are described in Figures 1 and 2, and in section 1A, 2a.

Procedure

The general technique for handling halogen fluorides and metal halides as performed in solvolysis reactions is described in section 1A, 2a.

In this investigation excess ClF_3 was placed into the nickel reactor, and the reactor agitated for 16 hours at room temperature. The product was then fractionated and characterized.

Result

This work was conducted to determine whether alkaline earth metal chlorides, in this case $MgCl_2$, would react with ClF_3 to form $Mg(ClF_4)_2$.

A reaction occurred to produce a white solid that did not react with water, and was only slightly soluble. It did not liberate I_2 from neutral potassium iodide solution. Analysis of the solid showed:

	Found	Theo. for $Mg(ClF_4)_2$	Theo. for MgF_2
Wt. % F	54.2	61.2	60.9

The fact that the solid did not liberate iodine from neutral aqueous potassium iodide and its observed lack of chemical reactivity or solubility with water, suggested that it was MgF_2. The $MgCl_2$ was converted to MgF_2 with no further reaction occurring. This observation is in agreement with the earlier study in which there was no reaction between MgF_2 and ClF_3.

c. $ClF_3 + BaF_2$

Material

BaF$_2$. J. T. Baker Chemical Co. Reagent Grade.

Apparatus

The general purpose metal high vacuum equipment and metal reactors are described in Figures 1 and 2 and in section 1A, 2a.

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Procedure

The general technique for handling halogen fluorides and metal halides in solvolysis reactions is described in section 1A, 2a.

In this study excess ClF_3 was placed in the reactor along with the BaF_2. The reactor was then agitated for 16 hours at 100°C. The products were then fractionated and characterized.

Results

In this investigation there was no evidence of a reaction. All of the BaF_2 and 98.8% of the ClF_3 were recovered. Since a reaction did not occur between BaF_2 and ClF_3, this adds credence to the conclusion that extensive solvolysis of a metal halide in a halogen fluoride can occur only if a volatile or reagent-soluble fluoride is formed (10).

     d. $ClF_3 + SrF_2$

Material

SrF_2. Allied Chemical and Dye Corporation, General Chemical Division, Reagent Grade.

Apparatus

The general purpose metal high vacuum equipment and metal reactors are described in Figures 1 and 2, and in section 1A, 2a.

Procedure

The general technique for handling halogen fluoride and metal halides in solvolysis reactions is described in section 1A, 2a.

The reactants, with ClF_3 in excess, were placed in the nickel reactor and agitated for 24 hours at 100°C. The product was then fractionated and characterized.

Results

The results of this study are described in Table 5. There was no evidence of a reaction under the conditions employed. Greater than 99% of the ClF_3 was recovered and the recovered SrF_2 showed only a slight increase in weight (0.5%), possibly due to absorbed ClF_3.

This observation is in general agreement with the data on MgF_2 and BaF_2 solvolysis reactions in ClF_3 (sections 1A, 3b and 3c) where no reaction occurred.

Strontium fluoride (like the alkaline earth metal fluorides MgF_2 and BaF_2) apparently does not undergo extensive solvolysis in ClF_3 by the formation of a volatile or reagent soluble fluoride.

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Table 5

Solvolysis of Alkaline Earth Halides in Chlorine Trifluoride

Expt. No.	Metal Halide	Quantity of Metal Halide (grams)	(moles)	Quantity of Chlorine Trifluoride (grams)	(moles)	Mole Ratio ClF₃/MF₂	Reactor Material	Reaction Temp. °C	Contact Time (hours)	Weight of Chlorine Trifluoride Removed From Reactor (grams)
1807D-81	BaF₂	8.807	0.056	61.30	0.664	11.8/1	Nickel	100	16	60.60
1807D-85	MgF₂	3.115	0.050	61.44	0.665	13.3/1	Nickel	100	16	61.67
1807D-91	MgCl₂	4.706	0.050	67.81	0.735	14.8/1	Nickel	Room Temp.	16	69.35
1876D-3	SrF₂	6.007	0.048	54.55	0.591	12.4/1	Nickel	100	24	54.29

Increase in Weight of MF₂ (grams)	Chemical Analysis	Remarks
None	-	-
None	-	-
-1.935	$F = 54.2 \pm 0.1\%$	The product, a white solid, did not react with, and was only slightly soluble in water. Product did not liberate iodine from neutral potassium iodide solutions. Results indicate that the MgCl₂ was converted to MgF₂, with no further reaction occurring. Approximately 100 p. s. i. g. gas pressure developed in the bomb during the reaction of the MgCl₂ with ClF₃.
0.033	-	> 99 per cent of input ClF₃ recovered at conclusion of experiment.

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e. $ClF_3 + MgF_2$ in BrF_5

Material

MgF$_2$. The Matheson Co., Matheson, Coleman and Bell Division, Reagent Grade.

BrF$_5$. Allied Chemical and Dye Corp., General Chemical Division.

Apparatus

The general purpose metal high vacuum equipment and metal reactors are described in Figures 1 and 2 and in section 1A, 2a.

Procedure

The general technique for handling halogen fluorides and metal halides in solvolysis reactions is described in section 1A, 2a.

In this experiment equimolar quantities of ClF_3 and BrF_5 were placed in the reactor with MgF_2. The solvent was in excess of the stoichiometric amount required for complete reaction. The reactor was then agitated for 24 hours at 100°C. The product was then fractionated and characterized.

Results

A reaction occurred between MgF_2 and the solvent system BrF_5-ClF_3 to produce a pale yellow solid mixed with the original MgF_2. The results are shown in Table 6. Since ClF_3 alone does not react with MgF_2 it was believed that the solid formed by the reaction of BrF_5 with MgF_2, as shown:

$$BrF_5 \rightleftharpoons BrF_4^+ + BrF_6^-$$

$$Mg^{++} + 2F^- + BrF_4^+ + BrF_6^- \rightleftharpoons Mg(BrF_6)_2 + 2BrF_5$$
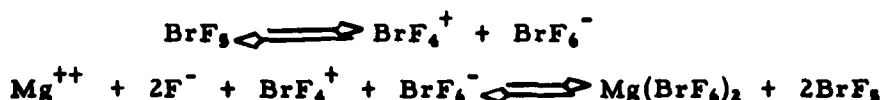
Approximately 5% conversion of MgF_2 to the polyhalide occurred based upon the weight increase of the recovered MgF_2. The unreacted MgF_2 could not be separated from the solid product. The resulting mixture, assuming that the converted MgF_2 existed as $Mg(BrF_6)_2$, would have a bromine content of 10.4%.

		Found	Theoretical for $Mg(BrF_6)_2$
Wt. %	Br	12.4 ± 0.1	38.8
	Cl	3.0 ± 0.1	0.0

In an attempt to overcome the insolubility (hence decreased solvolysis activity) of the alkaline earth metal fluorides the solvolysis of MgF_2 in the mixed solvent ClF_3-BrF_5 was investigated. This work was based on the premise that selected solvents might interact in such

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Table 6

Solvolysis of Magnesium Fluoride in Mixed Polyhalide System

Expt. No.	Grams of MgF_2	Halogen Fluoride	Quantity of Halogen Fluorides grams	moles	Mole Ratio Hal. F/MgF_2	Reactor Material	Reaction Temp. °C	Contact Time (hours)	Weight of Halogen Fluoride Removed from Reactor at 0°C (grams)
1807D-96	1.477 (0.024 moles)	BrF_3 ClF_3	77.6 41.5	0.445 0.449	18.8/1 19.0/1	Nickel	100	24	118.2

Increase In Weight
Of MgF_2 (grams)

0.423

Chemical Analysis
Of Product

Br = 12.4 ± 0.1%
Cl = 3.0 ± 0.1%

Remarks

Product was slightly yellow in color. An approximate
5 per cent conversion of MgF_2 to the polyhalide occurred
based upon weight increase. A theoretical bromine
content of 10.4 per cent was calculated for the mixture.
Polyethylene capsules were used for Parr bomb analysis.

a way as to alter their normal ionization characteristics.

Since only a small conversion to $Mg(BrF_6)_2$ occurred (based on the above assumptions), it appears that ClF_3 acted as a "base" in the BrF_5.

$$ClF_3 + BrF_5 \longrightarrow ClF_2^+ + BrF_6^-$$

4. Reactions with Group III Metal Fluorides

a. $ClF_3 + AlF_3$

Material

AlF_3. Allied Chemical and Dye Corp., General Chemical Division.

Apparatus

The general purpose metal high vacuum equipment and metal reactors are described in Figures 1 and 2, respectively, and in section 1A, 2a.

Procedure

The general technique for handling halogen fluorides and metal halides is described in detail in section 1A, 2a.

Excess ClF_3 was placed in the nickel reactor, Figure 2, with the AlF_3. The reactor was then agitated for 48 hours at 100°C. The product was then fractionated and analyzed.

Results

Results are listed in Table 7. This work was based on the premise that the following solvolysis reaction might occur, analogous to the reactions observed with the alkali metal fluorides, to form aluminum tetrafluoro-chlorate, $Al(ClF_4)_3$:

$$6ClF_3 \rightleftharpoons 3ClF_2^+ + 3ClF_4^-$$
$$AlF_3 \rightleftharpoons 3F^- + Al^{+++}$$

$$\overline{6ClF_3 + AlF_3 \longrightarrow Al(ClF_4)_3 + 3ClF_3}$$
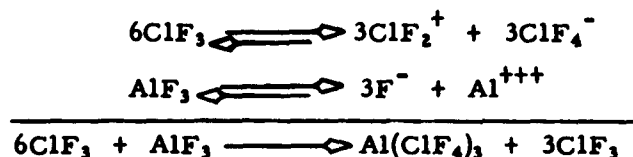
Apparently the solubility of aluminum fluoride is very low in chlorine trifluoride since most of the aluminum fluoride and greater than 96 per cent of the starting chlorine trifluoride were recovered. Based on the slight weight increase of the aluminum fluoride recovered and, if the assumption is made that the weight increase is due to conversion of AlF_3 to $Al(ClF_4)_3$, the maximum conversion is calculated to be 2.3%. There is no analytical evidence that $Al(ClF_4)_3$ was formed even in trace amounts. If a slight conversion did occur, then the yield might be increased by the use of mixed solvents or the adaptation of a special recycle system in which the desired $Al(ClF_4)_3$ could be removed continuously and thereby

Table 7

Solvolysis of Aluminum Fluoride in Halogen Fluorides

Experiment Number	Halogen Fluoride	Molar Reactants		Molar Ratio	Reaction Temp. °C	Contact Time hours	Weight of Halogen Fluoride Removed From Reactor at 0°C (grams)	Increase in Weight of AlF_3 (grams)	Total Halogen Fluoride Initially Charged to Reactor (grams)	Chemical Analysis of Product	Moles Reactants In Product	
		Halogen Fluoride	AlF_3								AlF_3	Halogen Fluoride
1876D-5	ClF_3	0.612	0.0502	12.2/1	100	48	54.759	0.324	56.596	None	0.0502	0.0035
1876D-7	BrF_3	0.902	0.0741	12.2/1	100	16	144.35	6.160	157.53	%Br=41.6	0.074	0.0353
1876D-10	BrF_3	0.640	0.0496	12.9/1	100	120	76.075	10.252	87.575	None	-	-

Remarks

Exp. No.

1876D-5   2.3% conversion of AlF_3 to $Al(ClF_4)_3$ based on weight increase.

1876D-7   Maximum 28.8% conversion AlF_3 to $Al(BrF_4)_3$ based on analysis.

1876D-10   Product contained liquid BrF_3; less than 50% conversion.

alter the equilibrium and force the reaction to completion.

      b.   <u>ClF_3 + BF_3</u>

<u>Material</u>

     ClF_3. The Matheson Co., Inc.

     BF_3. The Matheson Co., Inc.

<u>Apparatus</u>

    This work was conducted in the high pressure apparatus described in Figure 4. The autoclave was constructed of Monel metal.

<u>Procedure</u>

    Excess BF_3 was placed in the autoclave with the ClF_3. The reactants were held for 24 hours at 25°C. The material in the reactor was then fractionated at various temperatures to separate unreacted starting material and products.

<u>Results</u>

    This reaction was investigated to determine whether the compound $B(ClF_4)_3$ could be prepared.

    Results are shown in Table 8. A reaction occurred between ClF_3 and BF_3 to form a solid containing a 1:1 molar ratio of BF_3:ClF_3. Difficulty was experienced in removing the excess ClF_3 from the solid.

    Infrared examination of the solid showed bands at 1030 and 1070 cm^{-1}, characteristic of BF_4^- ion.

    Analysis showed:

		Found	Theoretical for $ClF_2^+BF_4^-$
Wt. %	B	7.12	6.8
	F	67.6	71.1
	Cl	<u>22.0</u>	<u>22.1</u>
		96.8	100.0

    Three possible molecular structures were postulated for the 1:1 addition compound:

    a. $ClF_3 \cdot BF_3$

    b. $ClF_2^+BF_4^-$

    c. $BF_2^+ClF_4^-$

Figure 4

High Pressure Assembly
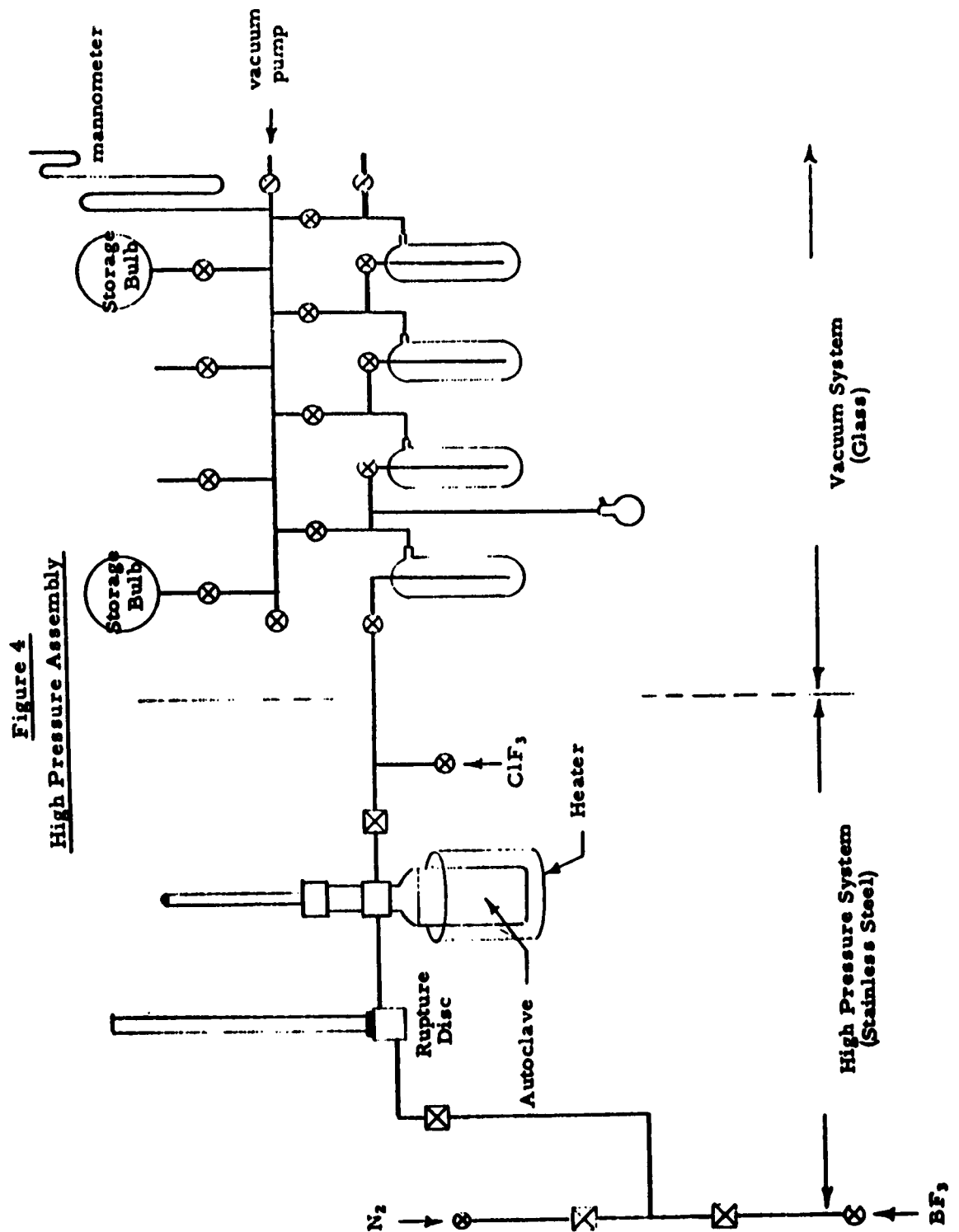
Table 8

Polyhalide Investigations

Of the three isomers, structure (b) was considered the most probable based on infrared data which showed the presence of bands at 1030 and 1070 cm^{-1}.

Several metathesis reactions were attempted with this new compound in an effort to determine the structure and to prepare new oxidizers. The reactions investigated, assuming that the structure is $[ClF_2^+BF_4^-]$, were:

a. $ClF_2^+BF_4^- + K^+ClO_4^- \longrightarrow ClF_2^+ClO_4^- + K^+BF_4^-$

b. $ClF_2^+BF_4^- + K^+ClO_3^- \longrightarrow ClF_2^+ClO_3^- + K^+BF_4^-$

c. $ClF_2^+BF_4^- + K^+NO_3^- \longrightarrow ClF_2^+NO_3^- + K^+BF_4^-$

d. $ClF_2^+BF_4^- + K_2^+NClO_3^= \longrightarrow (ClF_2)_2NClO_3 + 2K^+BF_4^-$

The results of this study did not confirm the structure although there was evidence for the formation of $K^+BF_4^-$. These reactions are discussed in detail in Section III.

c. $\underline{ClF_3 + AlF_3 + N_2O_4}$

Material

AlF$_3$. Allied Chemical and Dye Corp., General Chemical Division.

N$_2$O$_4$. The Matheson Co., Inc.

Apparatus

The general purpose metal high vacuum equipment and metal reactors are described in Figures 1 and 2, respectively, and in section 1A, 2a.

Procedure

The general procedure for handling halogen fluorides and metal halides is described in section 1A, 2a.

In this study, the reactants were placed in the reactor, and agitated at 25°C. for 24 hours.

Results

The primary objective of this investigation was to promote the formation of $Al(ClF_4)_3$ in the solvent N_2O_4:

$$3ClF_3 + AlF_3 \xrightarrow{N_2O_4} Al(ClF_4)_3$$

It was observed that alkali metal halides, namely CsF, RbF, and KF, react with ClF$_3$ to form the respective MClF$_4$ salts. The alkaline earth metal halides, as well as AlF$_3$, do not react with ClF$_3$ alone. In

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this study N_2O_4 was used to determine the effect of a mixed solvent on the reaction.

A reaction occurred to yield a solid. The results are listed in Table 9. Analysis of the solid showed the following elemental composition

		Found	Theoretical for $Al(ClF_4)_3$
Wt. %	Al	9.2	7.4
	N	12.6	0.0
	F	60.6	63.1
	Cl	3.7	29.4
	O	14.4	0.0
		100.5	99.9

Based on the high nitrogen and oxygen contents and the low chloride, it must be assumed that no $Al(ClF_4)_3$ was formed. Reaction between N_2O_4 and ClF_3 may have occurred

$$3N_2O_4 + 2ClF_3 \longrightarrow 6NO_2F + Cl_2$$
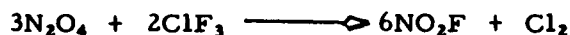
followed by subsequent interaction of the NO_2F with the AlF_3.

d. $ClF_3 + AlF_3 + CsF$
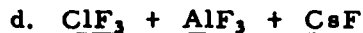
Apparatus

The general purpose metal high vacuum equipment and metal reactors were employed in this study.

Procedure

In this experiment a 1:1 mole ratio of AlF_3 and CsF was placed in the nickel reactor with excess ClF_3. The reactor was then agitated for 24 hours at 100°C.

Results

This experiment was conducted to determine the effect of mixed metal fluorides on solvolysis reactions in ClF_3. The reaction of CsF in ClF_3 is known to occur to produce $CsClF_4$.

In this case it was hoped that the presence of CsF might alter the reaction to produce $Al(ClF_4)_3$. A reaction occurred but only to a slight extent to form apparently $CsClF_4$. There was no evidence for the interaction of AlF_3. Results are listed in Table 9.

Table 9

PREPARATION OF FLUORIDES

Table 9a

Thermal Fractionation-Reaction Products - $NOClF_4$ + AlF_3 - Expt. No. 1089D-29

Wt. (g.) Fraction	Wt. Fraction Hydrolyzed	Temp. Fraction	Chemical %Cl	Analyses %F.	Moles(out) Cl	F	Moles(in) Cl	F
2.101	1.215	-79	78.6	26.5	0.046	0.029		
9.777	9.073	-23	35.1	40.1	0.097	0.206		
8.312	7.255	+25	35.1	38.9	0.082	0.170		
6.187	5.029	+136	0	47.1	0.00	0.154		
6.274		>+136	not analyzed					
Total 32.651					0.225	0.559	0.197	0.967

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5. Reactions with Nitrogen-Oxygen Compounds

Special emphasis was placed on the synthesis of nitrosyl and nitryl derivatives of the halogen fluorides. These compounds were expected to be more effective oxidizers than the analogous compounds in which the nitrosyl or nitryl cations were replaced by alkali or alkaline earth metals. A variety of compounds can be postulated as resulting from the reactions with nitrosyl fluoride (NOF), nitryl fluoride (NO_2F), and either bromine tri-fluoride (ClF_3), or bromine pentafluoride (BrF_5). These are shown below:
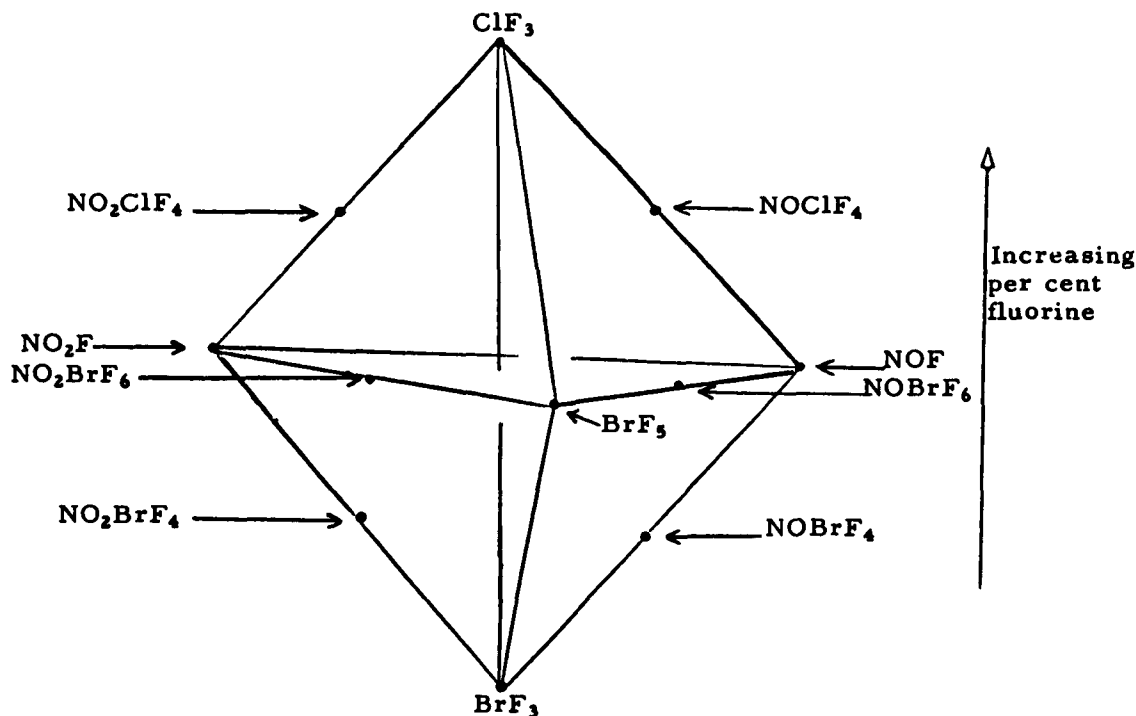
a. ClF_3 + NOF

Material

NOF. Nitrosyl fluoride was prepared by the method of Brauer (13). The apparatus is described in Figure 5. Elemental fluorine is passed into a Monel tube at the rate of 31 ml./minute. Before entering the reactor, the halogen is mixed with nitric oxide, the oxide entering at a rate of 65 ml./minute. The Monel tube requires slight external heating to initiate the reaction, then the reaction proceeds smoothly. The nitrosyl fluoride is collected in two nickel traps cooled to -120°C with ethyl bromide baths. Over a period of 5 hours, 31.6 grams (0.645 mole) of NOF was prepared which corresponds to approximately 80 per cent yield.

The nitrosyl fluoride was purified by low temperature vacuum fractionation. Comparison of the infrared spectrum of this material with

Figure 5

Apparatus for the Preparation of Nitrosyl Fluoride (NOF)

To Vent (Fisher Burner)

To liquid nitrogen trap, manometer and mechanical vacuum pump

-120°C. Traps

Monel Reactor

Fluorocarbon Bubble Off

Tube Furnace

Monel Tube containing NaF at 100°C. to remove HF from F_2
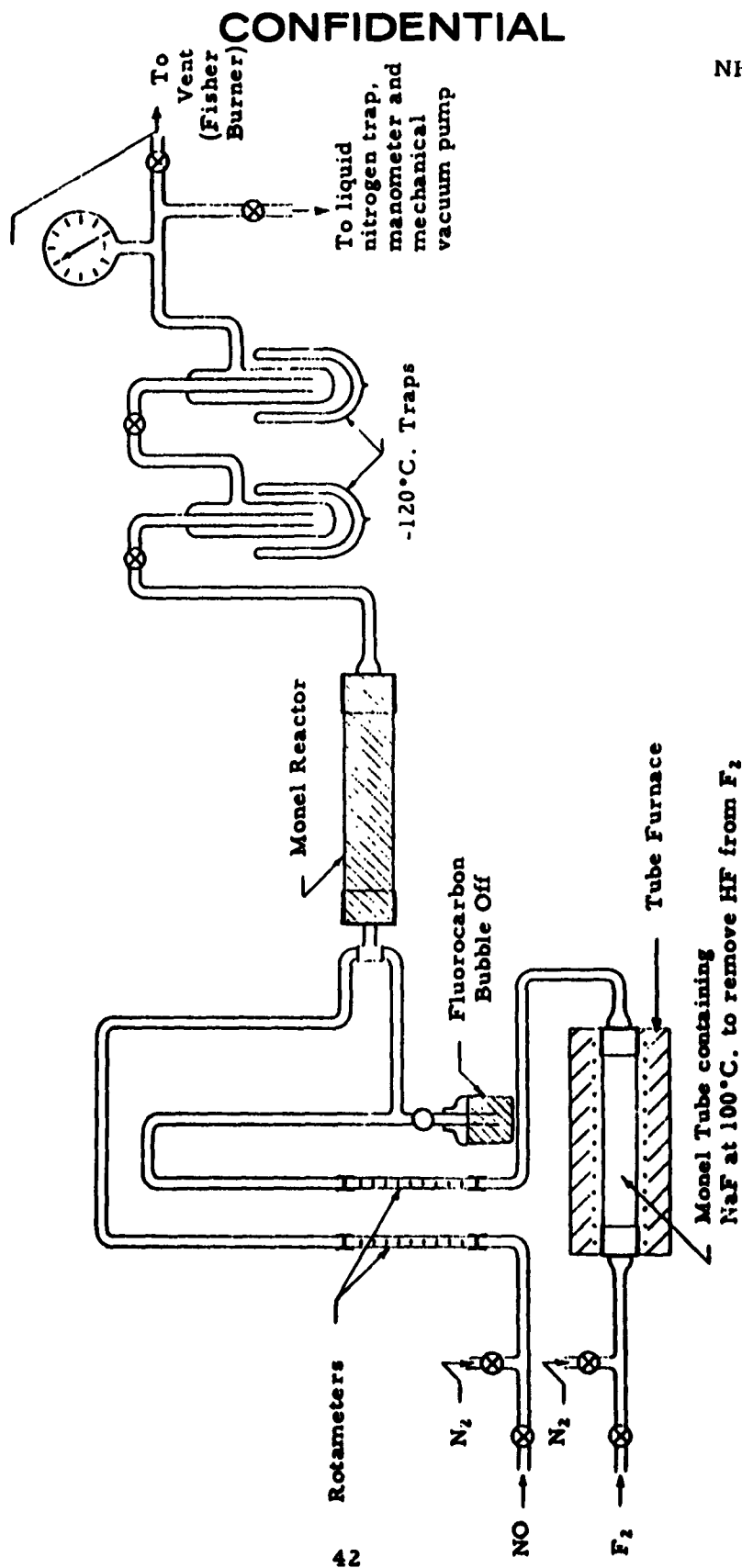
All lines are of 1/4" O.D. Copper Tubing

Rotameters

N_2

N_2

NO

F_2

the spectrum of a pure sample of NOF as given by Waltz et al (14) indicated that the nitrosyl fluoride was essentially pure, containing only a small amount of NO_2 and NO_2F. Total impurities were estimated to be 2 mole per cent.

Apparatus

The general purpose metal high vacuum equipment and metal reactors were used.

Procedure

Excess ClF_3 was placed in a nickel reactor with NOF. The reactor was then agitated for approximately 24 hours at -25°C.

Results

A reaction occurred between NOF and ClF_3 at -25°C. which resulted in the formation of a white solid. The elemental composition of this solid was:

		Found	Theoretical for $NOClF_4$
Wt. %	N	9.44 ± 0.24	9.90
	Cl	21.5 ± 0.1	25.07
	F	54.25 ± 0.05	53.7
	O	14.8 (by difference)	11.33
		100.0	100.00

Equilibrium dissociation pressures were determined for this material, Table 10, and from the shape of the log Kp vs. 1/T plot, a ΔH value of 15.8 Kcal. $mole^{-1}$ was calculated for the reaction:

$$NOClF_{4(s)} \rightleftharpoons ClF_{3(g)} + NOF_{(g)}$$

The plot log Kp vs. 1/T is shown in Figure 6.

After the decomposition the solid, obtained upon cooling to -78°C., was analyzed.

		Found
Wt. %	N	9.03 ± 0.23
	Cl	20.7 ± 0.1
	F	54.7 ± 0.2

From the above data and a value of -37.0 kcal. $mole^{-1}$ for the heat of formation of $ClF_{3(g)}$(15), and an estimated -9.0 kcal. $mole^{-1}$ for the

Figure 6

Plot of Log Kp vs. 1/T for the Reaction $NOClF_4(s) \rightleftharpoons NOF(g) + ClF_3(g)$

Temp. Range = 213-263° K.
Slope of Line = $-\Delta H/2.3R$

● Increasing temperature
○ Decreasing temperature

ΔH_R = +15 8 kcal. mol. $^{-1}$
Experiment 1737D-83

Log K_p

$1/T \times 10^3$
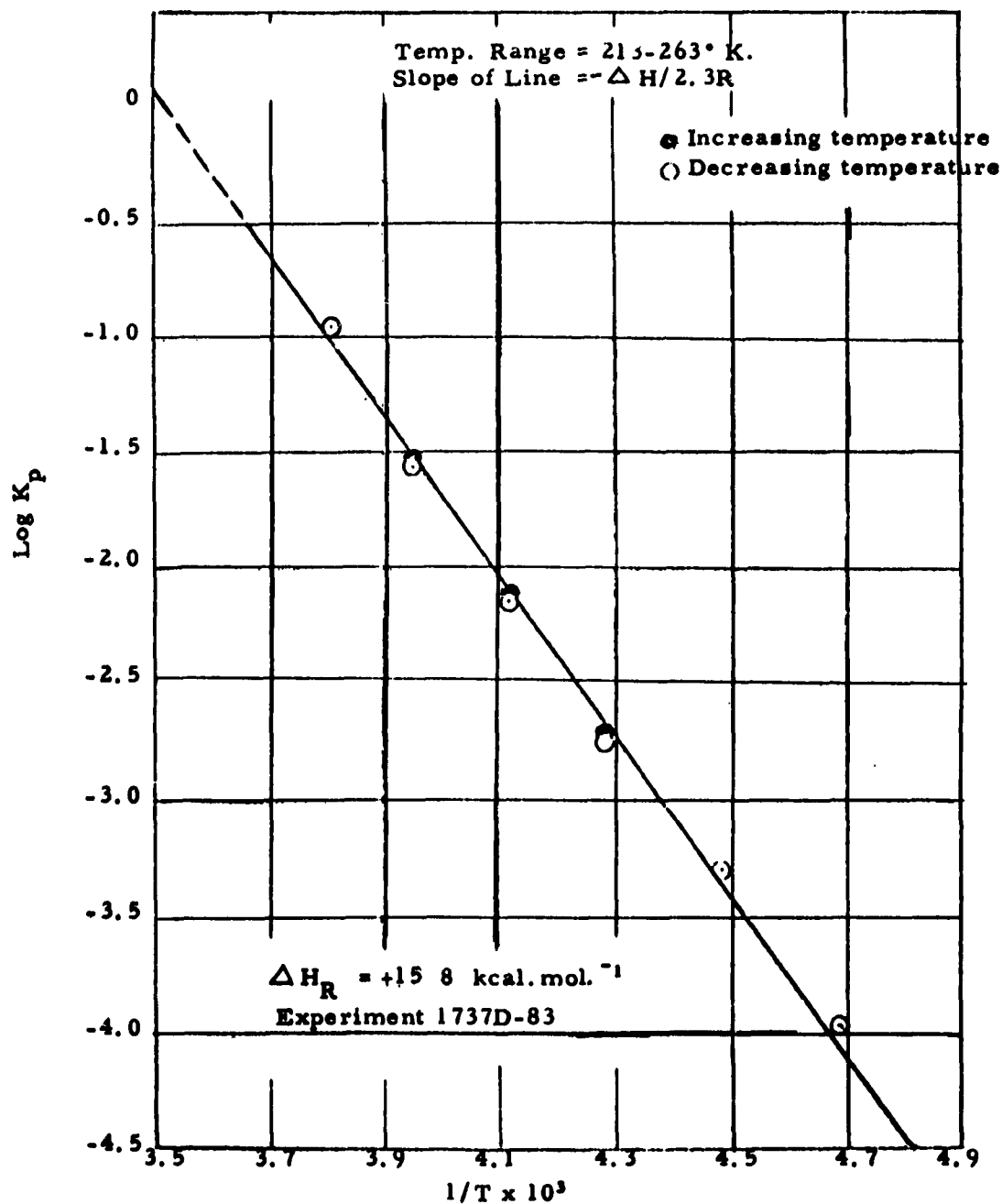
heat of formation of $NOF_{(g)}$(16), the following values for $NOClF_4$ were derived:

$$\Delta HF^\circ \ (298^\circ K) = 61.8 \ \text{kcal. mole}^{-1}$$

$$\Delta HF^\circ \ (298^\circ K) = 437 \ \text{cal. gram}^{-1}$$

The entropy of solid $NOClF_4$ was calculated to be 70.3 cal. deg^{-1} mole^{-1}, and a lattice energy value of 174 kcal. mole^{-1} was determined for this product.

It was not established wheter the product from the reaction of NOF and ClF_3 is simply a molecular complex. $NOF \cdot ClF_3$, a covalent compound, or an ionic nitrosyl salt of the hypothetical acid, $HClF_4$, i.e., $NO^+ClF_4^-$. Theoretical considerations indicate that the mechanism of the above reaction might be as follows:
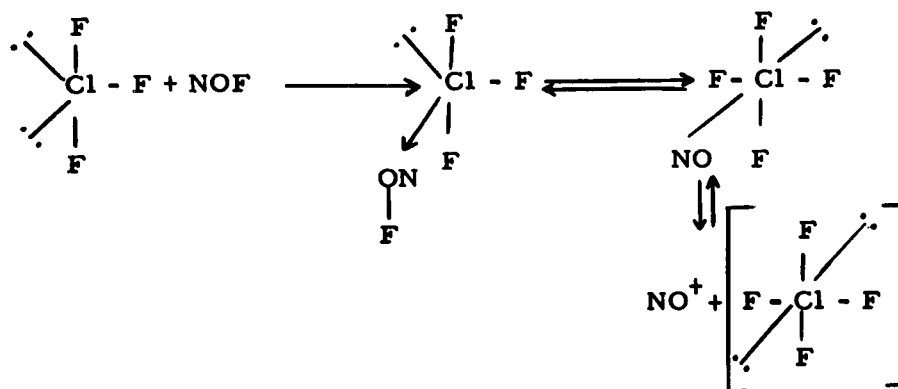
The above scheme is similar to a proposed mechanism for the exchange of fluorine between ClF_3 and HF (10) in which it was concluded that the experimental observations were consistent with the hypothesis that exchange proceeded through the formation of molecular complexes of the type:
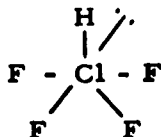
Thermal decomposition studies have shown that the reaction $NOF_{(g)} + ClF_{3(g)} \rightleftharpoons NOClF_{4(s)}$ is apparently reversible, the heat of dissociation of solid $NOClF_4$ into its gaseous constituents being approximately +15.8 kcal. mole^{-1}. This information should allow more accurate estimations of the heats of formation of compounds containing the ClF_4 group in their structure. More reliable specific impulse calculations can therefore be obtained on propellant systems employing the above type of

Table 10

Dissociation Pressure Data on the NOF-ClF$_3$ Reaction Product

Temperature		Increasing Temperature Measurements		Decreasing Temperature Measurements	
°C.	°K.	Pressure (atm.)	log K$_p$	Pressure (atm.)	log K$_p$
-60	213	0.0204	-3.98	—	—
-50	223	0.0442	-3.31	—	—
-40	233	0.0884	-2.71	0.0918	-2.68
-30	243	0.173	-2.13	0.177	-2.11
-20	253	0.340	-1.54	0.347	-1.52
-10	263	0.701	-0.91	—	—
0	273	1.37*	—	—	—

oxidizer.

The calculated lattice energy for $NOClF_4$, 174 kcal. $mole^{-1}$, is in the range that is expected for solid univalent metal halides (17). Based upon the calculated entropy change $(-55.5$ cal. $deg.^{-1}$. $mole^{=1})$, and the enthalpy change $(-15.8$ kcal. $mole^{-1})$ for the reaction:

$$NOF_{(g)} + ClF_{3(g)} \longrightarrow NOClF_{4(s)}$$
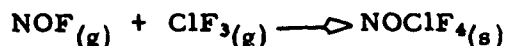
the free energy change (ΔF) may be expressed as:

$$\Delta F = -15,800 + 55.6 \ T \ cal. \ mole^{-1}$$

From the above, ΔF is equal to zero at 11°C., the boiling point of chlorine trifluoride at atmospheric pressure.

The entropy of formation of $NOClF_{4(s)}$ from its elements was determined,

$$1/2 Cl_{2(g)} + 2F_{2(g)} + 1/2 N_{2(g)} = 1/2 \ O_{2(g)} \longrightarrow NOClF_{4(s)} \qquad (I)$$
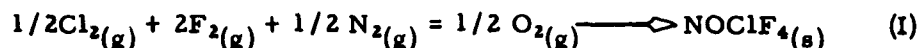
employing known values (15) for the entropies of the elements in their status:

$$\Delta F° (298°K) = 101 \ cal. \ deg.^{-1} \ mole^{-1}$$

The free energy of formation $\Delta F_f°$ of $NOClF_{4(s)}$ is obtained from the equation:

$$\Delta F° = \Delta H° - T\Delta S°$$

and is

$$\Delta F_f° - 31.7 \ kcal. \ mole^{-1} \ at \ 198°K$$

The equilibrium constant for reaction (I) at 298°K and one atmosphere pressure is given by:

$$K = exp \left[- \frac{\Delta F°}{RT} \right]$$

$$K \cong 1 \times 10^{23}$$

b. $ClF_3 + NO_2F$

NO_2F. Nitryl fluoride was prepared by the method of Aynsley, Hetherington, and Robinson (18). The apparatus is shown in Figure 7. This method is based on the reaction of $NaNO_2$ with fluorine. A stream of fluorine (approximately 4 g./hr.), diluted with nitrogen (1:1 by vol.), is passed over dry sodium nitrite. If the flow of nitrogen is excessive, a yellow flame results - probably due to nitrogen peroxide combustion in fluorine. This results in considerable attack on glass apparatus.

Figure 7

Apparatus for the Preparation of Nitryl Fluoride (NO₂F)
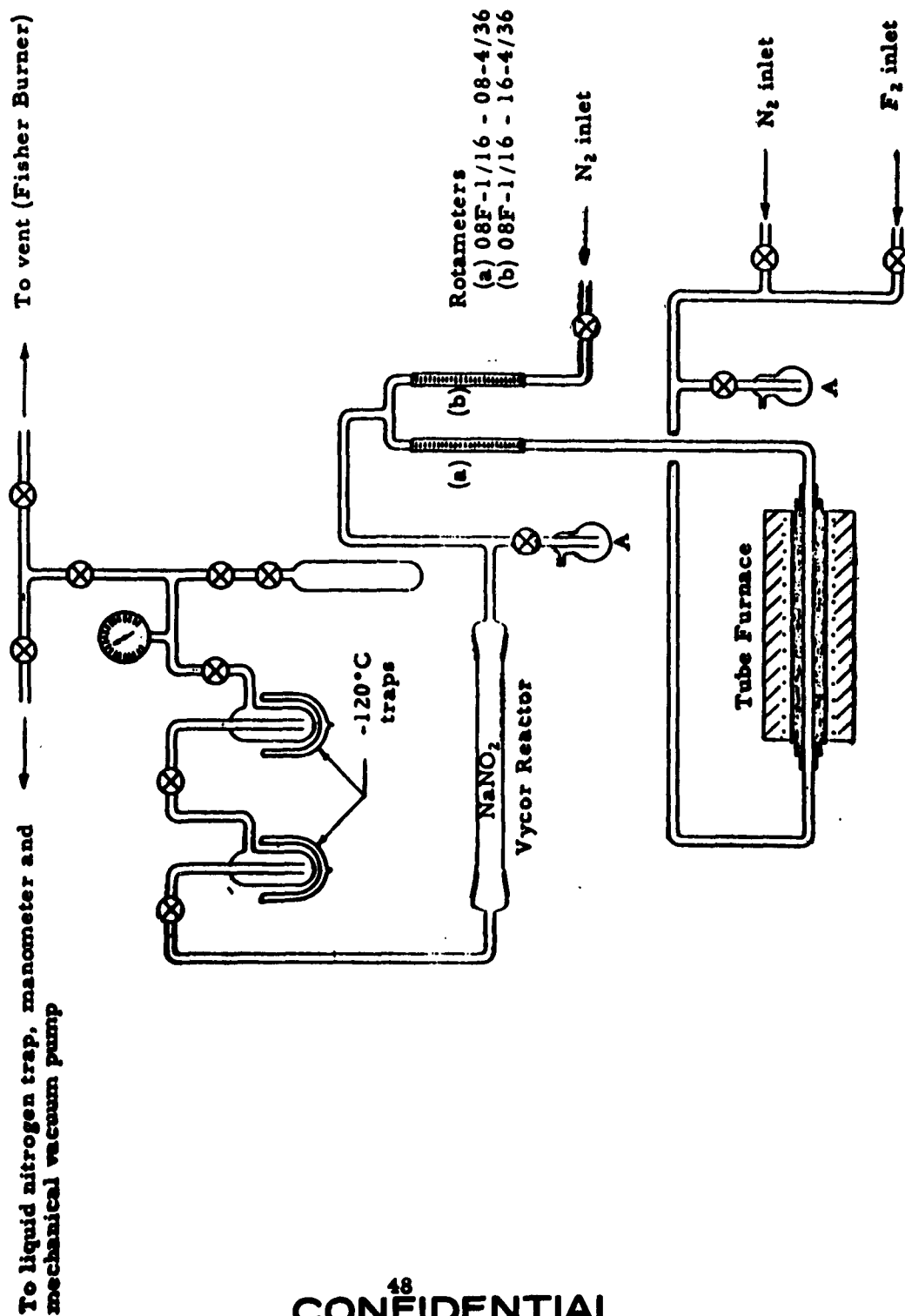
The gaseous product of the reaction of $NaNO_2$ with fluorine consists of nitryl fluoride contaminated with some nitrogen peroxide and fluorine. This gas was passed through traps cooled with melting ethyl bromide (-119°C.) where the NO_2F and N_2O_4 are collected while the fluorine is vented. The NO_2F was then fractionated from N_2O_4 by passing the gas through several traps cooled to -23°C. with melting carbon tetrachloride.

Apparatus

The general purpose vacuum line and metal reactor were used.

Procedure

In this experiment NO_2F and excess ClF_3 were placed in the reactor and held at 0°C. for 24 hours.

Results

Since a reaction was observed between NOF and ClF_3 (section 1A, 5a) to form a white solid,

$$NOF + ClF_3 \longrightarrow NOClF_4$$

it was postulated that a similar reaction might occur with NO_2F.

$$NO_2F + ClF_3 \longrightarrow\!\!\!\!\!\!/\!\!\!\!\longrightarrow NO_2ClF_4$$

In this case, however, there was no evidence of a reaction and the reactants were recovered unchanged. Since the solid $NOClF_4$ decomposes readily to NOF and ClF_3 it was assumed that NO_2ClF_4 may be even less stable and therefore was not detected. This investigation did not result in the detection or isolation of the expected product NO_2ClF_4.

The attempted synthesis of NO_2ClF_4 by metathesis reactions is discussed in section IIA, 1b, where evidence was obtained that NO_2ClF_4 is unstable at temperatures as low as -63°C.

c. $ClF_3 + N_2O_4$

Material

N_2O_4. The Matheson Co., Inc. No detectable impurities by infrared.

Apparatus

The apparatus consisted of a simple Teflon NMR tube 6 inches long, 1/2"OD and 1/4" ID. This Teflon tube was fitted with an aluminum needle valve with Teflon packing and attached to a metal high vacuum line.

Procedure

The ClF_3 and N_2O_4 were condensed into the Teflon NMR tube which

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had been cooled to -196°C. The reactants were then gradually warmed to -30°C. and a gas sample was removed for analysis. The tube was then recooled to -196°C. and placed in a low temperature F^{19} NMR probe. The tube was gradually warmed from -196°C. to 25°C. and scanned constantly for fluorine resonance signals.

Results

A Teflon NMR tube was used to prevent possible side reaction with metal or glass. In addition, if the reaction resulted in the formation of a possibly unstable compound such as ClF_2NO_2,

$$ClF_3 + N_2O_4 \rightleftharpoons ClF_2NO_2 + NO_2F$$

it was expected that its presence could be detected by low temperature F^{19} nuclear magnetic resonance.

A reaction did occur between ClF_3 and N_2O_4 at temperatures as low as -60°C. Infrared analysis of a gas sample which was collected while the tube was cooled to -30°C. showed the characteristic bands for NO_2F and N_2O_4.

A low temperature NMR scan from -196°C. to 25°C. detected only ClF_3. The chemical shift determined for the ClF_3 relative to Freon 11 (FC Cl_3) was -92.2 PPM. A sample of pure ClF_3 was then placed in the Teflon NMR tube and the chemical shift observed relative to Freon 11 was -103.8 to -92.6 PPM. In both cases the fluorine signal was very weak probably due to the shielding effect of the Teflon tube. The presence of NO_2F, or the expected product ClF_2NO_2, was not detected possibly due to the low concentrations present coupled with the shielding effect of the thick walled Teflon tube. The NO_2F, however, was detected by infrared. A possible reaction leading to the formation of NO_2F would be:

$$2ClF_3 + 3N_2O_4 \longrightarrow NO_2F + Cl_2$$

The reaction of ClF_3 with N_2O_4 also was investigated in a metal reactor. The results are shown in Table 9. Excess ClF_3 was placed in the reactor with N_2O_4 and the reactants permitted to stand at 25°C. for 6 hours. A large pressure rise was observed. The solid product recovered from the reactor contained nickel. Apparently extensive decomposition occurred resulting in the formation of stable nickel salt. There was no evidence for ClF_2NO_2, $ClF(NO_2)$, or $Cl(NO_2)_3$.

d. $ClF_3 + NOF + AlF_3$

Apparatus

The general purpose metal high vacuum equipment and metal reactors were used.

Procedure

Excess ClF_3, with equimolar quantities of AlF_3 and NOF, was placed in the nickel reactor and agitated at 80°C. for 72 hours.

Results

The objective of this study was to promote the following reactions:

$$3NOF + 3ClF_3 \longrightarrow 3NOClF_4$$

$$3NOClF_4 + AlF_3 \longrightarrow Al(ClF_4)_3 + NOF$$

It was postulated that a metathesis reaction might occur between $NOClF_4$ and AlF_3 in the mixed solvent $NOF-ClF_3$. In ClF_3, alone, AlF_3 does not react to produce $Al(ClF_4)_3$.

Results are shown in Table 11. Analysis of the solid isolated did not support the presence of $Al(ClF_4)_3$.

		Found	Theoretical for $Al(ClF_4)_3$	$NOClF_4$
Wt. %	Cl	0.0	29.4	25.1
	F	57.4	63.1	53.7
	N	6.1	0.0	9.9
	Al		7.4	0.0
	O		0.0	11.3
			99.9	100.0

The solid also contained iron apparently from ie interaction of the metal reactor system. The results of this study weir generally inconclusive although there was no evidence for the formation of $Al(ClF_4)_3$.

6. Other Reactions with ClF_3

a. $ClF_3 + SiF_4$

Material

SiF_4. The Matheson Co., Inc.

Apparatus

The general purpose metal high vacuum equipment and metal reactor were used.

Procedure

The ClF_3 (0.657 mole) and SiF_4 (0.107 mole) were condensed into the

Table 11

Reaction of Aluminum Fluoride, Nitrosyl Fluoride and Chlorine Trifluoride

or Bromine Pentafluoride

Expt. No.	Halogen Fluoride	Moles Reactants			Molar Ratio	Reaction Temp. °C	Contact Time (hours)	Increase in weight of AlF_3 (grams)	Chemical Analysis (per cent)				Empirical Formula	Remarks
		Halogen Fluoride	AlF_3	NOF					Cl	Br	F	N		
1876D-13	BrF_5	0.589	0.0496	0.232	12/1/4.7	25	72	18.853	-	27.1	41.1	8.26	$N_3AlBr_{1.a}F_{9.a}$	Total per cent 88.9. 11.7% iron present. Product reactive with water.
1876D-18	BrF_5	0.604	0.0500	0.201	12/1/4	80	72	34.900	-	37.9	42.5	3.57	$N_{1.5}AlBr_{1.a}F_{n.a}$	
1876D-23	ClF_3	0.72	0.05	0.05	1/1/14.4	80	72	3.0	0.0	-	57.4	6.1	-	Mixture of white and pale green crystals, not reactive towards water.
1876D-30	None	0.05	0.51		10/1	25	60	4.3	-	-	-	0.4	-	
1876D-34	ClF_3	0.84	0.05	0.27	6/1/17	-	-	7.8	-	-	64.7	11.6	$N_{2.a}AlF_{u}$	Total per cent 100.9. Product mildly reactive towards water.
1876D-34A	BrF_5	-	-	-	-	100	16	6.3	-	9.0	52.5	11.3	-	Total per cent 94.8. Product mildly reactive towards water. Starting material for this experiment was product from experiment 1876D-34.

nickel reactor which was then agitated for 20 hours at 160°C.

Results

The objective was to prepare the compound $Si(ClF_4)_4$ by the following hypothetical reaction:

$$SiF_4 + 4ClF_3 \longrightarrow Si(ClF_4)_4$$

Results are shown in Table 8. There was no evidence of a reaction and the reactants were recovered. If the reaction had occurred, the product was unstable under the conditions employed and decomposed to the initial reactants.

b. $ClF_3 + PF_5$

Material

PF_5. The PF_5 was prepared by the following reaction:

$$C_6H_5N_2PF_6 \xrightarrow{\quad 150°C. \quad} PF_5 + C_6H_5F + N_2$$
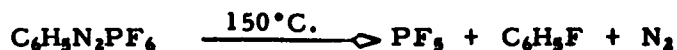
The resulting PF_5 was fractionated through a series of low temperature traps and identified by infrared.

Apparatus

Phosphorous pentafluoride (0.067 mole) and ClF_3 (0.678 mole) were condensed into a nickel reactor which was then agitated at 100°C. for 48 hours.

Results

This study was conducted to determine whether PF_5 would react with ClF_3 to form a phosphorous tetrafluorochlorate compound:

$$PF_5 + 5ClF_3 \rightleftharpoons P(ClF_4)_5$$

The results are shown in Table 8. The weight fractions and their infrared analyses indicated the possible existence of a complex between PF_5 and ClF_3 stable at approximately -20°C. or below. The results were inclusive and $P(ClF_4)_5$, or any other (ClF_4) compound of phosphorous, was not isolated.

c. $ClF_3 + PF_3$

Material

PF_3. Phosphorous trifluoride was prepared by the method of C. J. Hoffman (19) by the reaction of PCl_3 with AsF_3. The crude PF_3 was fractionated by passing the vapors through traps cooled to -80 and -196°C. The PF_3 was identified by its infrared spectrum.

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Apparatus

  The general purpose metal high vacuum equipment and metal reactor were used.

Procedure

  Phosphorous trifluoride (0.081 mole) and ClF_3 (0.691 mole) were condensed into the nickel reactor which was then agitated at 100°C. for 24 hours.

Results

  This reaction was investigated to determine whether PF_3 would react with ClF_3 to form a tetrafluorochlorate by the following reaction:

$$PF_3 \; + \; 3ClF_3 \; \xleftrightarrow[\text{24 hours}]{100°C.} \; P(ClF_4)_3$$
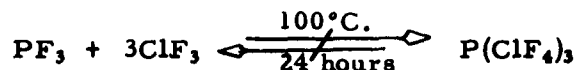
The results are shown in Table 9. A reaction occurred to produce PF_5 and an unidentified substance which showed a complex infrared spectrum with absorption bands at 792, 786, 757 and 749 cm.$^{-1}$. The desired product, $P(ClF_4)_3$, was not isolated nor identified.

d. $ClF_3 \; + \; SF_4$

Material

  SF_4. E. I. duPont de Nemours and Co., Inc. Technical Grade. The SF_4 contained 4-6% sulfuryl fluoride. This SF_4 was used as received.

Apparatus

  The general purpose metal high vacuum line and metal reactor were used.

Procedure

  Chlorine trifluoride (0.825 mole) and sulfur tetrafluoride (0.156 mole) were condensed into the reactor and agitated for 16 hours at 100°C.

Results

  The objective of this investigation was to prepare a tetrafluoro-chlorate by the following postulated reaction:

$$SF_4 \; + \; 4ClF_3 \; \xleftrightarrow[\text{16 hrs.}]{100°C.} \; S(ClF_4)_4$$
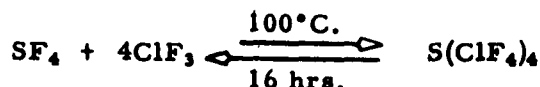
The results are shown in Table 9. Fractionation of the product did not result in the complete recovery of SF_4. Infrared analysis of the fractions

collected at 0°C. and -95°C. showed complex patterns with bands at 11.0, 11.6 and 11.7 microns in addition to major absorption bands which were attributed to SF_6. Apparently a reaction occurred in which S^{IV} was oxidized to S^{VI}. The desired product, $S(ClF_4)_4$, was not isolated nor detected.

e. $ClF_3 + Mg(SO_4)_2$

Material

MgSO$_4$. Mallinckrodt Chemical Works. Anhydrous, analytical grade.

Apparatus

The general purpose metal high vacuum line and nickel reactor were used.

Procedure

Chlorine trifluoride (0.756 g. mole) and anhydrous magnesium sulfate (0.042 g. mole) were placed in the reactor and agitated for 16 hours at 100°C.

Results

In solvolysis reactions with chlorine trifluoride and various multi-valent metal fluorides, reactions did not occur to produce tetrafluorochlorate salts. It was therefore decided to investigate the reaction of an anhydrous salt containing an anion other than fluorine. Magnesium sulfate was selected and the desired reaction was:

$$MgSO_4 + 4ClF_3 \quad \xrightarrow{\quad 100°C. \quad} \quad Mg(ClF_4)_2 + (ClF_2)SO_4$$
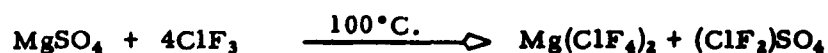
The results are shown in Table 9. The loss in weight of $MgSO_4$ solid indicated that some reaction had occurred possibly to form MgF_2. The desired product, $Mg(ClF_4)_2$, was not isolated nor detected.

Essentially the same results were obtained when this reaction was repeated. The analytical data supported the formation of MgF_2 rather than the desired product $Mg(ClF_4)_2$. The results are shown in Table 12.

f. $ClF_3 + Mg(BF_4)_2$
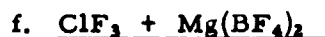
Material

$Mg(BF_4)_2$. Magnesium tetrafluoroborate was prepared by the reaction $MgF_2 + BF_3 \xrightarrow[\quad 25°C. \quad]{\quad HF \quad} Mg(BF_4)_2 + HF$.

Apparatus

The general purpose metal high vacuum line and metal reactor were used.

Table 12

Preparation of Polyhalide Salts of Multivalent Elements Solvolysis Reactions

Exp. No.	Reactants A moles	B	moles	Molar Ratio A/B	Weight increase (g) of Product over reactant	Results
109D-76	MgSO₄ 0.04	ClF₃	0.76	1/18	-2.13 over MgSO₄	NO Mg(ClF₄)₂ produced - most MgSO₄ converted to MgF₂
109D-78	Mg(BF₄)₂ 0.08	ClF₃	0.76	1/9.7	+0.20 over Mg(BF₄)₂·1.2HF	Mg(ClF₄)₂ was not produced to any extent. A weight increase of 3.86 g. would be necessary for 100% conversion-chemical analysis of product %Cl = 3.1, %F = 71.1, %B = 10.9

Procedure

Chlorine trifluoride (0.76 g. mole) and $Mg(BF_4)_2$ (0.08 g. mole) were placed in the reactor and agitated for 16 hours at 25°C.

Results

The solvolysis of $Mg(BF_4)_2$ in ClF_3 was investigated with the expectation that greater solubility in the interhalogen ClF_3 might occur to produce a reaction. The desired reaction was

$$Mg(BF_4)_2 + 4ClF_3 \longrightarrow Mg(ClF_4)_2 + 2ClF_2BF_4$$
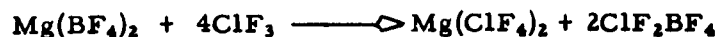
The results are shown in Table 12. A slight increase of magnesium product should result if reaction occurred. A slight weight increase was observed but magnesium tetrafluorochlorate was not detected. Analysis indicated that the product was principally unreacted magnesium tetrafluoroborate.

		Found	Theoretical for $Mg(BF_4)_2$
Wt%	Cl	3.1	0.0
	F	71.1	76.8
	B	10.9	10.9

A weight increase of 3.86 g. of magnesium product would be expected if all of the $Mg(BF_4)_2$ were converted to $Mg(ClF_4)_2$. The observed weight increase was 0.20 g. This slight increase could be due to absorption of ClF_3, or some unknown impurity, on the $Mg(BF_4)_2$. There was no evidence for the formation of $Mg(ClF_4)_2$ under the conditions employed.

B. Reactions with BrF_3

1. Objective

The primary objective of this task was to prepare new fluorine solid oxidizers of the type $M(BrF_6)x$ where M=alkali metal, alkaline earth metal, aluminum, the nitrosyl cation NO^+, or the nitryl cation NO_2^+. While compounds containing the hexafluorobromate ion were not expected to meet the high impulse specifications of this program, their density, stability and reactivity would serve as guides to the synthesis of the more energetic solid fluorine oxidizers.

Just as the solvolysis of metal halides in both ClF_3 and BrF_3 resulted in the formation of ClF_4^- and BrF_4^- derivatives, so it was expected that BrF_6^- compounds would form if BrF_5 were used. While no such compounds had yet been prepared at the start of this work, it was a reasonable assumption that similar solvolysis reactions would occur.

$$2BrF_5 \rightleftharpoons BrF_4^+ + BrF_6^-$$
$$MF \rightleftharpoons M^+ + F^-$$

$$2BrF_5 + MF \rightleftharpoons M^+BrF_6^- + BrF_5$$
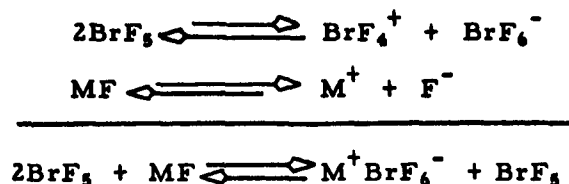
It was noted that metals with smaller ionic radii were less reactive with chlorine trifluoride and that the thermal stability of the corresponding alkali metal tetrafluorochlorates decreased as the ionic radii decreased. The alkaline earth metal fluorides were found to be less reactive with chlorine trifluoride than were the alkali metals.

Similar trends were expected in the solvolysis reactions of metal fluorides in bromine pentafluoride.

The fluorination of alkali metal hydroxides, alkaline earth metal oxides and alkali metal peroxides with bromine pentafluoride also was investigated. Cady (27) had reported that the reaction of fluorine with alkali metal hydroxides resulted in the liberation of oxygen. We postulated that the solvolysis of metal hydroxides in bromine pentafluoride might result in the formation of metal hypofluorites rather than metal fluorides and oxygen.

$$2BrF_5 + 2MOH \longrightarrow 2MOF + 2BrF_3 + 2HF$$

The BrF$_5$ used in this study was obtained from the General Chemical Division of the Allied Chemical and Dye Corporation. Prior to use it was purified by being passed through a Monel tube containing NaF pellets at 100°C. to remove traces of HF and BrF$_3$ and then vacuum fractionated to remove any fluorine present.

Unless specified otherwise, the apparatus consisted of the general purpose metal high vacuum line and reactor shown in Figures 1 and 2, respectively.

2. Reactions with Group I Metal Fluorides

a. BrF$_5$ + NaF

Material

NaF. The Matheson Co., Matheson, Coleman and Bell Division. The NaF was dried before use by heating under vacuum at 110-120°C. for 16 hours.

Procedure

Sodium fluoride (0.080 mole) and bromine pentafluoride (0.960 mole) were placed in the reactor and agitated for 63 hours at 140°C.

Results

This reaction was investigated to determine whether sodium hexafluorobromate ($NaBrF_6$) could be prepared by the solvolysis of NaF in BrF_5.

$$2BrF_5 \rightleftharpoons BrF_4^+ + BrF_6^-$$

$$BrF_4^+ BrF_6^- + Na^+ + F^- \longrightarrow NaBrF_6\downarrow + BrF_5$$
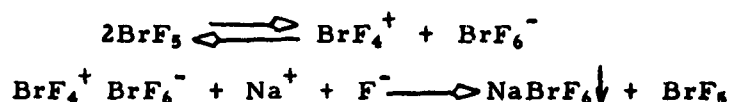
Based upon the weight of solid product recovered, a 4.6% conversion of NaF to $NaBrF_6$ had occurred. The composition of the solid was calculated as $NaBrF_6 \cdot 2aNaF$. Since the conversion of NaF to $NaBrF_6$ was small, even after 63 hours of reaction time, this reaction was not investigated further.

b. $BrF_5 + KF$

Material

KF. Allied Chemical and Dye Corp., General Chemical Division. The potassium fluoride was dried before use by heating under vacuum at 110-120°C. for 16 hours.

Procedure

Potassium fluoride (0.078 mole) and bromine pentafluoride (0.810 mole) were placed in the reactor and agitated for 72 hours at 100°C.

Results

The experimental conditions and results are shown in Table 13. This work was conducted to determine whether the solvolysis of KF in BrF_5 would result in the formation of $KBrF_6$ by the following reaction:

$$2BrF_5 \rightleftharpoons BrF_4^+ + BrF_6^-$$

$$BrF_4^+ + BrF_6^- + K^+ + F^- \xrightarrow[\text{72 hrs.}]{100°C.} KBrF_6\downarrow + BrF_5$$
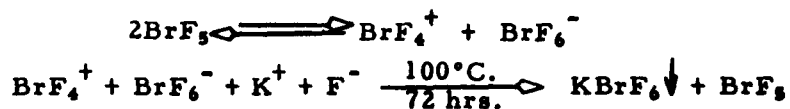
Based upon weight of solid product recovered, a 49.4% conversion of KF to $KBrF_6$ had occurred, resulting in a crude solid product with the composition $KBrF_6 \cdot KF$. Analysis of this crude product showed:

		Found	Theoretical for $KBrF_6 \cdot KF$
Wt. %	Br	25.2 ± 0.2	27.3
	F	43.5 ± 0.3	45.8
	K	-	26.9
			100.0

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Table 13

Solvolysis Reactions Between Alkali Metal Fluorides and Bromine Pentafluoride

Experiment No.	Quantity of BrF_5 grams	moles	Metal Fluoride (MF)	Quantity of MF grams	moles	Mole Ratio MF	BrF_5	Reactor	Reaction Temp. (°C)
1807D-23	141.5	0.810	KF	4.52	0.078	1	10.4	Nickel	106
1807D-27	167.9	0.960	NaF	3.37	0.080	1	11.9	Nickel	140

Experiment No.	Contact Time (hours)	Weight of Product (grams)	Analysis (%) Br	F	Remarks
1807D-23	72	11.23	25.2±0.2	43.5±0.3	Based upon weight of product, a 4.4% conversion of KF to $KBrF_6$ had occurred giving a material with the composition $KBrF_6 \cdot KF$ (I) Theoretical for (I): Br=27.3%; F=45.4%
1807D-27	63	4.021	-	-	Based upon weight of product, only a 4.6% conversion of NaF to $NaBrF_6$ had occurred giving a material with the composition: $NaBrF_6 \cdot 2lNaF$.

It is interesting to note that the solvolysis of KF in a mixed solvent of BrF_5 with ClF_3 produced $KClF_4 \cdot 0.74$ KF rather than $KBrF_6$ (Section 1A, 2g). In the absence of ClF_3, KF reacts with BrF_5 to form $KBrF_6$. In each case the metal fluoride behaved as a base.

c. $BrF_5 + RbF$

Material

RbF. American Potash and Chemical Corp. The rubidium fluoride was dried before use by heating under vacuum at 110-120°C. for 16 hours.

Procedure

Rubidium fluoride (0.0791 mole) and bromine pentafluoride (0.355 mole) were placed in the reactor and agitated for 16 hours at 100°C.

Results

The objective of this investigation was to prepare the compound $RbBrF_6$ by the following reaction:

$$BrF_5 \longrightarrow BrF_4^+ + BrF_6^-$$

$$Rb^+ + F^- + BrF_4^+ + BrF_6^- \xrightarrow{-100°C} RbBrF_6 \downarrow + BrF_5$$
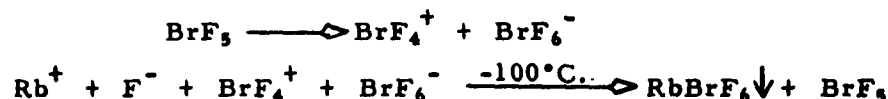
Based on the weight of solid product recovered the composition of the solid was calculated to be $RbBrF_6 \cdot 0.1RbF$, assuming that RbF was converted to $RbBrF_6$. Analysis of the solid showed:

		Found	Theoretical for $RbBrF_6 \cdot 0.1RbF$
Wt. %	Br	27.2	27.7
	F	39.8	40.0

Based on the weight of recovered solid a 92.5% conversion of RbF to $RbBrF_6$ occurred. It is interesting to note that $RbClF_4$ (section 1A, 2d) is light pink while $RbBrF_6$ is white.

d. $BrF_5 + CsF$

Material

CsF. American Potash and Chemical Corp. The cesium fluoride was dried by heating under vacuum at 110-120°C. for 16 hours. Emission spectrographic analysis indicated that it contained between 0.005-0.05% silicon.

FC-75. Minnesota Mining and Manufacturing Co., Manufacturer describes Fluorochemical FC-75 as a completely fluorinated cyclic ether.

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Procedure

Cesium fluoride (0.0513 mole) and bromine pentafluoride (0.170 mole) were placed in the reactor and agitated for 20 hours at 100°C.

Results

This work was conducted to determine whether cesium hexafluoro-bromate could be prepared by the following reaction:

$$2BrF_5 \rightleftharpoons BrF_4^+ + BrF_6^-$$

$$CsF \xrightarrow{100°C.} F^- + Cs^+$$

$$\overline{2BrF_5 + CsF \longrightarrow CsBrF_6\downarrow + BrF_5}$$
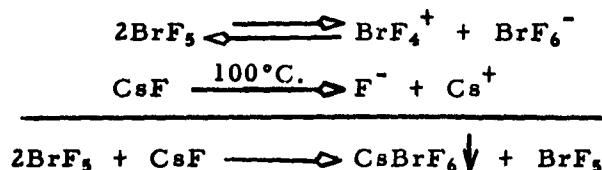
A reaction occurred to produce a white solid that reacted vigorously with water and liberated iodine from aqueous potassium iodide solution.

Analysis of the solid supported the formation of $CsBrF_6$.

		Found	Calculated
Wt. %	Br	24.4 ± 0.1	24.4
	F	34.8 ± 0.1	34.9

X-ray diffraction studies were made with a Norelco unit manufactured by the North American Phillips Co., with a cameral diameter of 114.59 mm. The samples were mounted in Pyrex capillary tubes and irradiated at room temperature with $CuK\alpha$ radiation at 35K volts and 18 ma. Radiation wave length (λ) = 1.5405 A. The X-ray data for two CsF-BrF_5 products are shown in Table 14. This data was compared to published data for cesium fluosilicate (20). In the table, d-spacings as calculated from Bragg angle data and crystal lattice constants (a) and reflection intensities (I) from various crystal planes (h, k, l) are given for each compound. Inspection of Table 3 shows that the patterns obtained for the product from two experiments are consistent with the published data for cesium fluosilicate. This might be due to a reaction of the glass capillary with $CsBrF_6$ to form Cs_2SiF_6.

Thermal decomposition studies on $CsBrF_6$ indicate that this material is unusually stable as compared to alkali metalpolyhalide compounds in general. It may be hypothesized that $CsBrF_6$ has a high percentage of ionic character in the metal-halide bonds. This may be due in part to (a) the relatively low ionization potential of cesium as compared to the other members of the alkali series, and (b) to the highly electronegative nature of the BrF_6^- anionic group. In any case, it appears that bromine pentafluoride is not bound in this compound by simple Van der Waal forces. The thermal stability of $CsBrF_6$ is shown in Table 15. It does not decompose even when heated to 360°C.

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Table 14

Comparison of X-ray Data on CsBrF$_6$ with that for Cesium
Fluosilicate as given by National Bureau of Standards

h, k, l	Cs$_2$SiF$_6$ (cubic) Cu, 1.5405A° 25°C., (NBS)			CsF-BrF$_5$ Product Cu, 1.5405A° 25°C., exp. 1807D-7			CsF-BrF$_5$ Product Cu, 1.5405A° 25°C., exp. 1740D-31		
	d A°	I	a A°	d A°	a A°	I	d A°	I	a A°
111	5.16	26	8.93				5.03	w	8.71
200	4.47	62	8.93	4.22	8.44	s	4.44	s	8.88
220	3.15	100	8.92	2.99	8.46	vs	3.16	vs	8.94
311	2.69	1	8.93						
222	2.576	48	8.92	2.45	8.49	s	2.53	s	8.76
400	2.231	26	8.92	2.12	8.48	s	2.19	s	8.76
420	1.996	25	8.92	1.90	8.50	s	1.96	s	8.77
4.22	1.821	19	8.92	1.74	8.52	s	1.80	s	8.82
511	1.717	4	8.92						
440	1.577	9	8.92	1.51	8.54	w	1.56	m	8.82
600	1.487	9	8.92	1.42	8.52	w	1.47	m	8.82
620	1.4099	10	8.917				1.40	m	8.85
622	1.3442	6	8.916	1.35	8.95	w	1.33	w	8.82
444	1.2872	3	8.918	1.29	8.94	w	1.28	vw	8.87
711	1.2486	1	8.917						
640	1.2364			1.24	8.94	w	1.23	w	8.87
642	1.1918			1.19	8.91	w	1.18	m	8.83
731	1.1610								
800	1.1147	1	8.918						
820	1.0814	4	8.918	Average of last 4 values 8.94			1.07	w	8.82
822	1.0509	4	8.917				1.04	w	8.82
751	1.0294	1	8.915						
662	1.0228	2	8.917				1.02	vw	8.89
840	1.9968	4	8.916				0.992	w	8.87
842	.9731	2	8.919				.968	w	8.87
664	.9506	4	8.917				.947	w	8.88
844	.9102	1	8.918				.907	w	8.89
10.0.0	.8918	1	8.918				.888	s	8.88
10.2.0	.8746	6	8.919				.872	w	8.89
10.2.2	.8582	1	8.919						
10.4.0	.8281	1	8.919	Average of last 5 lines 8.919			.825	s	8.89
10.4.2	.8141	2	8.918				.812	s	8.96

w=weak   vw=very weak   s=strong   vs=very strong   Average 8.86

m=medium

Table 15

Chemical Analysis of Cesium Hexafluobromide ($CsBrF_6$) after Thermal Treatment

Material	Bromine (%)	Fluorine (%)
Theoretical for $CsBrF_6$	24.4	34.8
Salt prepared in experiment 1807D-7	14.4 ± 0.1	34.8 ± 0.1
Salt prepared in experiment 1807D-7 after heating to 360°C.	24.5 ± 0.1	32.2 ± 0.1

A density determination was made by the pycnometer method (21) using Fluorochemical FC-75 as the displaced liquid. The observed value was 3.68 g. ml.$^{-1}$.

With the exception of the questionable X-ray data, due to possible reaction with the glass capillary, the data support the formation of an adduct of CsF with BrF$_5$.

3. Reactions with Group II Metal Halides

a. BrF$_5$ + BaF$_2$

Material

BaF$_2$. J. T. Baker Chemical Co., Reagent Grade

Procedure

Barium fluoride (0.049 mole) and bromine pentafluoride (0.740 mole) were placed in the reactor and agitated for 16 hours at 100°C.

Results

This reaction was conducted to determine whether Ba(BrF$_6$)$_2$ could be prepared by the following reaction:

$$4BrF_5 \rightleftharpoons 2BrF_4^+ + 2BrF_6^-$$

$$BaF_2 \rightleftharpoons 2F^- + Ba$$

$$\overline{4BrF_5 + BaF_2 \longrightarrow Ba(BrF_6)_2 + 2BrF_5}$$
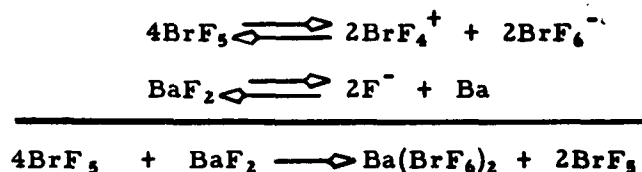
While the alkali metal halides reacted with bromine pentafluoride, there was no evidence of a similar reaction with barium fluoride. In this case there was no weight gain of solid product over the initial barium fluoride added and 99.5% of the initial bromine pentafluoride added was recovered. The results are shown in Table 16.

The alkaline earth metal fluorides also were found to be less reactive with ClF$_3$ than the alkali metal fluorides. This trend seems to apply to the alkaline earth metal fluorides in bromine pentafluoride.

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Table 16

Solvolysis of Alkaline Earth Halides in Bromine Pentafluoride

Expt. No.	Metal Halide	Quantity of Metal Halide grams	moles	Quantity of Bromine Pentafluoride grams	moles	Mole Ratio BrF_5/M_2	Reactor Material	Reaction Temp. °C	Contact Time (hours)	Weight of Bromine Pentafluoride Removed From Reactor at 0°C (grams)	Increase in Weight Of M_2 (grams)	Chemical Analysis of Product
1807D-83	BaF_2	8.523	0.049	129.2	0.740	15.2/1	Nickel	100	16	128.6	None	-
1807D-86	MgF_2	3.055	0.049	125.9	0.720	14.7/1	Nickel	100	16	123.4	1.864	-
1807D-93	MgF_2	1.511	0.024	142.4	0.815	33.6/1	Nickel	150	40	140.3	0.842	$Br=13.2\%$
1807D-88	$MgCl_2$	4.846	0.051	89.50	0.512	10.0/1	Nickel	Room Temp.	16	90.22	-1.513	$F=56.6\pm0.0\%$ $Br=9.25\pm0.11\%$
1807D-102	SrF_2	6.236	0.050	84.98	0.486	9.8/1	Nickel	100	64	84.27	None	-

Remarks

Weight increase indicates that a 10.9 per cent conversion of MgF_2 to a magnesium polyhalide had taken place. Product was a yellow solid, reactive with water giving a strong positive potassium iodide test.

Based upon weight increase of the MgF_2, a 9.9% conversion of MgF_2 to magnesium polyhalide was obtained. The product was a yellow solid which ignited gelatine capsules. Poly-ethylene capsules were then used for Parr Bomb analysis. A theoretical bromine content of 16.3 per cent was calculated for the mixture.

Approximately 50 p. s. i. g. gas pressure developed in the bomb during the reaction of the $MgCl_2$ with BrF_5. Mass spectrographic analysis revealed that this gas contained a considerable amount of chlorine. Results indicate that a 100% conversion of $MgCl_2$ to MgF_2 occurred followed by a 7.56% conversion of MgF_2 to magnesium polyhalide. Based upon the assumption that all the bromine was present in the product as the hexa-fluorobromate (V) ion, mixed with unreacted MgF_2, a theoretical fluorine content of 58.5 per cent was calculated for the mixture.

$>$99 per cent of input BrF_5 recovered at conclusion of experiment.

b. $BrF_5 + MgCl_2$

Material

MgCl$_2$. J. T. Baker Chemical Co., Reagent Grade

Procedure

Magnesium chloride (0.051 mole) and bromine pentafluoride (0.512 mole) were placed in the reactor and agitated for 16 hours at approximately 25°C.

Results

The objective of this work was to prepare $Mg(BrF_6)_2$ by the following reaction:

$$4BrF_5 \rightleftharpoons 2BrF_4^+ + 2BrF_6^-$$

$$MgCl_2 \rightleftharpoons 2Cl^- + Mg^{++}$$

$$4BrF_5 + MgCl_2 \longrightarrow Mg(BrF_6)_2 + 2BrF_3 + 2FCl$$
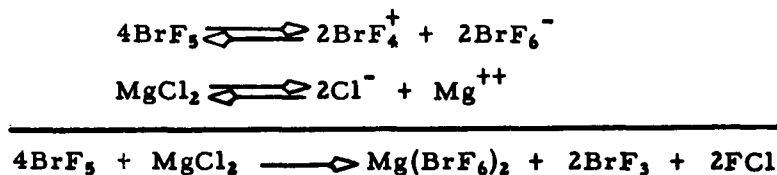
A complex reaction occurred which resulted in the evolution of chlorine. The results are shown in Table 16. Apparently the magnesium chloride was converted to the fluoride and the fluoride then reacted with the bromine pentafluoride:

$$MgCl_2 + BrF_5 \longrightarrow MgF_2 + BrF_3 + Cl_2$$

$$MgF_2 + 2BrF_5 \longrightarrow Mg(BrF_6)_2$$
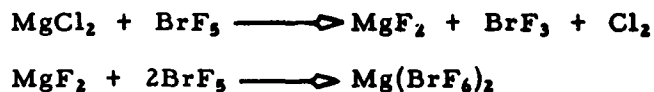
If the assumption is made that all of the magnesium chloride was converted to the fluoride and the fluoride in turn reacted with the bromine pentafluoride to form $Mg(BrF_6)_2$ to the extent of 7.56%, the theoretical fluorine content of the crude solid product would be 56.5%. This value is in reasonable agreement with the fluorine content found by analysis.

		Found
Wt. %	F	56.0 ± 0.0
	Br	9.25 ± 0.1

When MgF$_2$ was reacted with BrF$_5$ (see below) a 10% conversion

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of MgF_2 to a magnesium polyhalide occurred. These values are in the range for the calculated conversion of 7.56% in this experiment.

The fluorination of $MgCl_2$ was not unexpected since a similar reaction occurred when $MgCl_2$ was reacted with chlorine trifluoride (Section 1A, 3b). Magnesium chloride was fluorinated to the corresponding fluoride by reaction with the chlorine trifluoride.

c. $BrF_5 + MgF_2$

Material

MgF_2. The Matheson Company Inc., Matheson, Coleman and Bell, Division Reagent Grade.

Procedure

Magnesium fluoride and excess bromine pentafluoride were placed in the reactor and agitated at 100-150°C. for 16 hours.

Results

This reaction was conducted to determine whether magnesium fluoride would react with bromine pentafluoride as follows:

$$4BrF_5 \rightleftharpoons 2BrF_4^+ + 2BrF_6^-$$

$$MgF_2 \rightleftharpoons Mg^{++} + 2F^-$$

$$\overline{MgF_2 + 4BrF_5 \longrightarrow Mg(BrF_6)_2 + 2BrF_5}$$
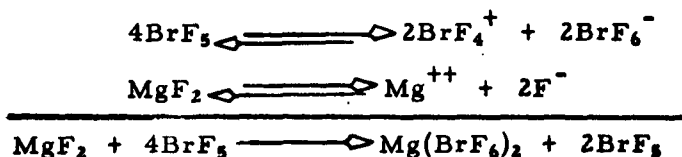
A reaction occurred to produce a yellow solid that reacted vigorously with water and liberated iodine from aqueous potassium iodide solution. The results of two experiments are shown in Table 16.

If the conversion of magnesium fluoride to $Mg(BrF_6)_2$ occurred as shown in the equation above, the theoretical weight of solid product could be calculated based on the weight of magnesium fluoride added initally. The actual weight increase of solid product corresponded to 10.9 and 9.9% conversion of the available magnesium fluoride to $Mg(BrF_6)_2$. For the crude solid product obtained in experiment 1807D-93, Table 16, the calculated bromine content based on weight changes was 16.3%. The actual content was 13.2%.

Incomplete conversion of the magnesium fluoride to the magnesium polyhalide complicates the precise characterization of the polyhalide. Normal purification techniques involving hydrocarbon solvents or water could not be used due to the reactivity of these polyhalides.

In this study it can be reasonably concluded that a reaction occurred to the extent of about 10% to yield a reactive magnesium polyhalide.

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The density of $Mg(BrF_6)_2$ was calculated by the molar volume method (22):

$$P = \frac{M}{\mathcal{E}\,Vi}$$

Where M = molecular weight of the compound

$\mathcal{E}\,Vi$ = sum of ionic volumes = $\mathcal{E}\,4/3\,\pi\,r^3$

r = ionic radius expressed in Angstrom units.

The structure of $Mg(BrF_6)_2$ was taken to be the same as magnesium fluoride, i.e., tetragonal. The density was calculated to be 2.60 g. cm^{-3}, Table 17. The values of atomic radii used in these calculations are listed in Table 22.

d. BrF_5 + SrF_2

Material

SrF_2. Allied Chemical and Dye Corp., General Chemical Division Reagent Grade.

Procedure

Strontium fluoride (0.050 mole) and bromine pentafluoride (0.486 mole) were placed in the reactor and agitated for 64 hours at 100°C.

Results

This study was conducted to determine whether a strontium poly-halide could be prepared by the following reaction:

$$4BrF_5 \rightleftharpoons 2BrF_4^+ + 2BrF_6^-$$

$$SrF_2 \rightleftharpoons Sr^{++} + 2F^-$$

$$4BrF_5 + SrF_2 \xrightarrow{\ 100°C.\ } Sr(BrF_6)_2 \downarrow + 2BrF_3$$
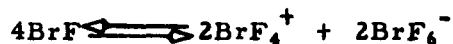
There was no evidence of a reaction. Greater than 99% of the bromine pentafluoride was recovered and all of the strontium fluoride was recovered. The results are shown in Table 16.

In the alkali metal series the reactivity with BrF_5 appeared to increase with increasing cationic size

		% Conversion of Metal Fluoride	
NaF	4.6	MgF_2	10%
KF	49.4	SrF_2	0
RbF	92.5	BaF_2	0
CsF	100		

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Table 17

Density Calculations

Compound	Experimental Density	Calculated	
		Molar Volume Method	Unit Cell Method
CsBrF$_6$	3.68 g. cm^{-3}	3.32 g. cm^{-3}	3.30 g. cm^{-3}
MgF$_2$	3.0	2.82	*
NO$_2$BrF$_6$	-	2.37	2.33
Mg(BrF$_6$)$_2$	-	2.60	*

* Insufficient data for calculations

whereas there was no evidence of reaction with the heavier alkaline earth metal fluorides of barium and strontium. A 10% conversion, however, was obtained with the smaller atomic radius metal, magnesium.

The marked difference in chemical reactivity between the alkali metal fluorides and the alkaline earth metal fluorides was also observed in reactions with chlorine trifluoride. Solvolysis reactions of metal fluorides in chlorine trifluoride and bromine pentafluoride apparently are affected by ionic size as well as ionization potential

4. Reactions with Group I Metal Hydroxides

a. BrF_5 + NaOH

Material

NaOH. Mallinckrodt Chemical Works. Analytical Grade, Purity 98%

Apparatus

A special Teflon reactor, Figure 8, was used for this investigation.

Procedure

This reaction was investigated in both a static and a flow system. In the static system sodium hydroxide (0.6 gram) and bromine pentafluoride (5 grams) were charged to the reactor described in Figure 8. The reactants were then warmed from -196°C. to 25°C. The product was then fractionated and analyzed.

In the flow system (Experiment 1860D-35, Table 18) sodium hydroxide (0.6 g.) was placed in the reactor, Figure 8, and bromine pentafluoride diluted with nitrogen passed over the sodium hydroxide at 25°C. The gaseous product was collected in a series of Monel traps cooled to -10°C., -78°C. and -196°C.

Results

The objective of this study was to prepare alkali metal hypofluorites by the following fluorination reaction.

$$NaOH + BrF_5 \xrightarrow{\quad 25°C. \quad} NaOF + HF + BrF_3$$

In the static system only a small amount of oxygen was liberated. There was no evidence of extensive reaction.

When bromine pentafluoride gas diluted with nitrogen was passed over solid sodium hydroxide the sodium hydroxide turned orange-red in color, but there was no evidence of extensive reaction with the bromine pentafluoride.

The results of this work, shown in Table 18, were generally

Figure 8

Specially Fabricated Teflon Reactor Used in Experiments 1860D-37 through 45

METAL INSERT TOP he ld by attachment w/bolts through reactor and bottom plate

Metal Plate Bottom

Teflon Reactor

Table 18

MOH + BrF$_5$ $\longrightarrow$ MOF + HF + BrF$_3$
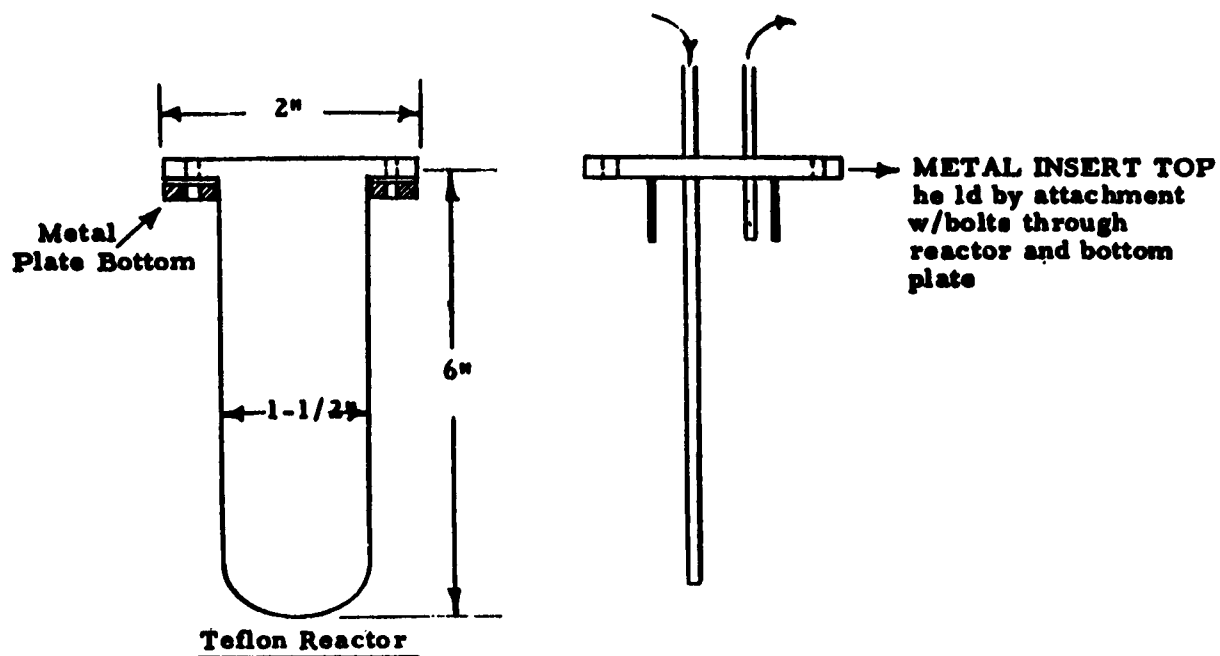
Experiment Number	Reactants (g)	Reaction Temperature °C	Analysis			Remarks
			(Solid Product) % F	% Br	Gaseous Product	
1860D-27[a]	BrF$_5$ (10) + KOH (0.6)	-195 to 25	64.8	neg.	predominately O$_2$	Slight reaction w/KI solution. Solid gave off HF upon standing. Reaction occurred between -5 - 20°C. Solid product not homogenous.
1860D-29[a]	BrF$_5$ (10) + LiOH (0.8)	-195 to -5	38.3	neg.	predominately O$_2$	Positive KI test
1860D-43	BrF$_5$ (10) + LiOH (1.0)	-78 to 0	37.0	16.4 (Ionic F$^-$ 0.18)	predominately O$_2$ Trace OF$_2$	When solid product was heated to 80°C there was no apparent decomposition. Slight reaction w/KI solution.
1860D-35	BrF$_5$ (gas) + NaOH (0.6) Flow system	-78	Solid not analyzed - orange red in color			Attempted pretreatment to remove impurities. Unsuccessful.

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inconclusive. Cady (27) reported the liberation of oxygen by the reaction of alkali metal hydroxides with fluorine. When sodium hydroxide was added to liquid bromine pentafluoride a small amount of oxygen was liberated. (Experiment 1860D-25). A possible reaction scheme leading to the formation of oxygen is:

$$2BrF_5 + NaOH \longrightarrow NaBrF_6 + BrF_3 + HF + 1/2 \, O_2$$

b. BrF_5 + KOH

Material

KOH. Mallinckrodt Chemical Works, Purity 85%.

Apparatus

The Teflon reactor, Figure 8, was used in this study.

Procedure

Potassium hydroxide (0.6 g.) and bromine pentafluoride 10 g.) were placed in the reactor. The reactants were then slowly warmed from -196°C. to 25°C. The product was then fractionated and analyzed.

Results

This work was conducted to determine whether potassium hypofluorites could be prepared by the reaction of potassium hydroxide with bromine pentafluoride, i.e.:

$$KOH + BrF_5 \longrightarrow KOF + BrF_3 + HF$$
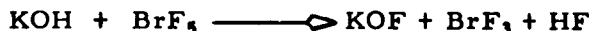
A reaction occurred in the temperature range -5°C. to 20°C. with evolution of oxygen. Partial analysis of the solid showed:

		Found	Theoretical for		
			KF.HF	KOF.HF	KOF
Wt. %	F	64.8	50.0	40.4	25.6
	Br	0.0	0.0	0.0	0.0

Results were inconclusive due to difficulty in fractionating the solid for precise characterization. The evolution of oxygen, however, indicated that KOF was probably not present in the solid product. Experimental results are shown in Table 18.

c. BrF_5 + LiOH

Material

LiOH. Mallinckrodt Chemical Co., Anhydrous, Reagent Grade.

Apparatus

The Teflon reactor, Figure 8, was used in this experiment.

Procedure

Lithium hydroxide (0.8 g.) and bromine pentafluoride (10 g.) were placed in the reactor and then warmed from -196°C. to -5°C. The product was then fractionated and analyzed.

Results

The objective of this work was to determine whether lithium hypofluorite could be prepared by the following reaction:

$$LiOH + BrF_5 \xrightarrow{-5°C.} LiOH + BrF_3 + HF$$
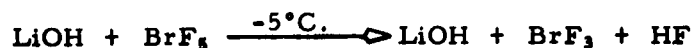
A reaction occurred at about -5°C. as evidenced by the evolution of oxygen. Evolution of oxygen, of course, is discouraging since this indicates possible decomposition. Analysis of the crude solid showed fluorine contents of 38.3 and 37.0 weight per cent as shown in Table 18, but the bromine content was zero and 16.4 weight per cent, respectively. These products were undoubtedly contaminated with HF and unreacted lithium hydroxide. The only significant data obtained in this work was the evolution of oxygen. The composition of the solid product was not established.

5. Reactions with Metal Oxides

a. BrF₅ + MgO

Material

MgO. J. T. Baker Chemical Co., Reagent Grade

Procedure

Magnesium oxide (1.2 g.) and bromine pentafluoride (13.8 g.) were placed in the reactor and permitted to stand at 100°C. for several hours. The product was then fractionated.

Results

Since the fluorination of metal hydroxides with bromine pentafluoride resulted in liberation of oxygen, the fluorination of metal oxides was investigated to determine whether the corresponding metal hypofluorites could be synthesized. In this case the following reaction was postulated:

$$MgO + BrF_5 \xrightarrow{100°C.} Mg(OF)_2 + BrF_3$$
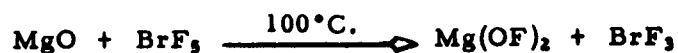
Results are shown in Table 19. Apparently some fluorination occurred since the recovered solid product contained 11.3 weight %

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Table 19

Investigation of Reactions of Bromine Pentafluoride and Group II A Metal Oxides

Experiment No.	Reactants Compd.	Weight Cmpd. g.	Weight g.	Temperature Initial °C	Temperature Final °C	Pressure Initial psig	Pressure Final psig	Gain in Weight of Solid Product	Volatiles at -78°C	Volatiles at Room Temp.	Analysis of Solid Product %F	%Br
1860D-3 (a)	MgO 95% purity	1.2	BrF₅	13.8 (Approx.)	-196	100	0	35 at 100°C	? color white	?	orange-red v.p. 203 min. at 90°C	11.3	Not Anal.
1860D-7 (b)	CaO 85-86% purity	3	BrF₅	16.6 (Approx.)	-196	25	0	25	? color tan, white	color: solid yellow white-small amount	orange-red	42.8	8.8
1860D-11 (c)	CaO	2.90	BrF₅	21.6	-196	22	0	65	? color tan, white	infra-red anal. showed NO₂ unknown bands at 2.5-2.7 and 5.5-5.84	lost due to air leakage		
1860D-13 (d)	CaO	2.960	BrF₅	21.168	-196	25	0	65	pumped to const. weight 1.817 g color tan, white	Mass spec. anal. O₂, trace CO₂	v.p. greater than atm. at room temp. deep orange red		
1860D-16 (e)	BaO₂ 88%	1.723	BrF₅	21.424	-196	27	0	17	NOT COMPLETED				

REMARKS

(a) Oxal. Solid Prod. Did not react with HOH. Did not fume in air. Negative KI

(b) Oxal. Solid Prod. Did not react with HOH. Did not fume in air. Positive KI

(c) Same as above.

(d) Did not react with HOH. Fumed in air. Bromine color prevalent. Positive KI Strong.

(e) Not Completed.

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fluorine. This solid did not react with water and did not liberate iodine from aqueous potassium iodide solution.

There was no evidence that magnesium hypofluorite was formed in this experiment. The inert nature of the recovered solid suggested a mixture of unreacted magnesium oxide and magnesium fluoride.

b. $BrF_5 + CaO$

Material

CaO. Fisher Scientific Company, Reagent Grade.

Procedure

In a typical experiment 3 grams of CaO and 20 grams of BrF_5 were placed in the reactor and then slowly warmed from -196°C. to 25°C. and allowed to stand for several hours at 25°C. The product was then fractionated.

Results

The results of these experiments are shown in Table 19.

It was reasoned that since metal hydroxides liberate oxygen when fluorinated with BrF_5 and the generated HF complicates fractionation and analysis of the final product, more information might be obtained by fluorinating metal oxides. The objective of this work was to prepare calcium hypofluorite. The expected reaction was:

$$CaO + BrF_5 \longrightarrow Ca(OF)_2 + BrF_3$$

There was evidence of a slight reaction, possibly with impurities, that resulted in the formation of small amounts of oxygen. Initially it was thought that a reaction occurred since the recovered solid showed a significant weight gain over the initial weight of calcium oxide added. It was later demonstrated that this weight gain was merely due to incomplete removal of unreacted BrF_5. There was no evidence of a significant reaction or for the presence of calcium hypofluorite.

c. $BrF_5 + BaO_2$

Material

BaO_2. Allied Chemical and Dye Corp., General Chemical Division, Technical Grade.

Procedure

Barium peroxide (1.7 g.) and bromine pentafluoride (21 grams) were placed in the reactor and then warmed slowly from -196°C. to 27°C. and permitted to stand at 27°C. for several hours.

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Results

This work was a section of the overall plan to prepare metal hypofluorites by the fluorination of metal hydrides, metal oxides and metal peroxides.

In this case the following reaction was postulated:

$$BaO_2 + BrF_5 \longrightarrow Ba(OF)_2 + BrF_3$$

The results are shown in Table 20. A slight pressure increase was observed at 27°C. and the recovered solid showed a weight increase of 0.031 g. over the 1.7 g. of BaO_2 added initially. Analysis of the solid showed 6.1 weight % fluorine and 1.6 weight % bromine. This analysis suggests a small amount of bromine pentafluoride merely absorbed on the barium peroxide and possibly contaminated with a small amount of metal fluoride. There was no evidence of extensive reaction or the formation of the desired product.

d. $BrF_5 + Na_2O_2$

Material

Na_2O_2. Fisher Scientific Company, Reagent Grade, Purity 981 %

Procedure

In a typical experiment 3 grams of sodium peroxide and 30 grams of bromine pentafluoride were placed in the reactor. The reactants were then warmed from -196°C. to 25 or 50°C. and allowed to stand for 20 hours.

Results

This work was part of the overall exploratory plan to determine if metal hypofluorites could be prepared by the fluorination of metal hydroxides, metal oxides and metal peroxides. The postulated reaction was:

$$Na_2O_2 + BrF_5 \longrightarrow NaOF + BrF_3$$

The results of this investigation are shown in Table 20. Some reaction occurred that resulted in the liberation of oxygen. This was observed also with the metal hydroxides. In this case the unreacted sodium peroxide was recovered and weighed. Slight weight gains over the starting sodium peroxide were noted. Analysis of the solid product showed:

		Found	
		1860-19	1860-23
Wt. %	F	8.5	5.2
	Br	0.3	0.3

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Table 20

Reactions of Bromine Pentafluoride with Oxides and Peroxides

Experiment Number	Reactants (g)	Temperature Initial °C	Final °C	Pressure (psig) Initial	Final	Analysis %Br	%F	Gain in Weight of Solid (g)	Remarks
1860D-15	BrF₅ 21.4 BaO₂ 1.7	-196	27	0	17	1.6	6.1	0.031	
1860D-19	BrF₅ 27.8 Na₂O₂ 2.6	-196	25	0	5	0.3	8.5	0.183	Product gas identified as O₂
1860D-23	BrF₅ 30.7 Na₂O₂ 3.4	-196	50	0	10	0.3	5.2	0.22	Product gas identified as predominantly O₂

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Some fluorination had apparently occurred, but the liberation of oxygen was not encouraging and this work was discontinued. The presence of fluorine in the solid was probably due to sodium fluoride which could have formed by the following reaction:

$$Na_2O_2 + BrF_5 \longrightarrow 2NaF + O_2 + BrF_3$$

6. Reactions with NOF and NO₂F

a. BrF₅ + NOF

Material

NOF. Nitrosylfluoride was prepared by the method of Brauer (13) by the reaction of fluorine with nitric oxide.

Procedure

NOF and excess BrF₅ were condensed into the nickel reactor and allowed to stand at -25°C for 16 hours.

Results

While considerable success was achieved in the synthesis of metal hexafluorobromates, these polyhalides are not highly energetic oxidizers. The nitryl and nitrosyl derivatives were expected to be more energetic. This work was directed toward the preparation of NOBrF₆ by the reaction:

$$BrF_5 + NOF \longrightarrow NOBrF_6$$

but, at 25°C., there was no evidence of a reaction.

b. BrF₅ + NO₂F

Material

NO₂F. Nitryl fluoride was prepared by the method of Aynsley, Hetherengton and Robinson (18) by the reaction of sodium nitrite with fluorine.

Procedure

Nitryl fluoride (9. 267 g., 0. 1427 mole) and bromine pentafluoride (18. 276 g., 0. 1045 mole) were condensed into the nickel reactor, warmed to room temperature and agitated by mechanical rocking for 16 hours.

Results

The purpose of this work was to determine whether nitryl hexafluoro-bromate (NO₂BrF₆) could be prepared by the reaction:

$$BrF_5 + NO_2F \longrightarrow NO_2^+ \ BrF_6^-$$

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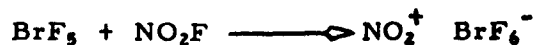
At 25°C. there was no evidence of a reaction. Of the 9.267 grams of nitryl fluoride added, 8.920 g. or 96.3% was recovered. The recovery of BrF_5 was 18.645 g. or 102.1%. They were identified by vapor pressure and their infrared spectra.

There was no evidence for the formation of the desired NO_2BrF_6. If the compound did form, it may have decomposed at 25°C. to the starting reactants:

$$NO_2BrF_6 \rightleftharpoons NO_2F + BrF_5$$

The density of the theoretical NO_2BrF_6 was calculated both by the molar volume method and the method based upon unit cell size. Since hard sphere assumptions were used in both cases, the density values calculated are nearly the same. The accuracy of the two methods was evaluated by comparison of calculated and known densities for the salts $CsBrF_6$ and MgF_2.

The molar method is (2):

$$\rho = \frac{M}{Vi}$$

where M = molecular weight of the compound

$$\xi\ Vi = \text{sum of ionic volumes} = \xi\ 4/3\ \pi\ 4^3$$

r = the ionic radius expressed in Angstrom units

The unit cell calculation is (27):

$$\rho = \frac{1.6602\ \xi A}{V}$$

where A = sum of atomic weights in unit cell

V = volume of unit cell in cubic A

The crystal structure of NO_2BrF_6 was assumed to be the same as postulated for $CsBrF_6$ i.e., simple cubic. The calculated densities by the molar volume method and by the unit cell method were 2.37 and 2.33 g./cc. respectively. The results of several calculations are listed in Table 17. The values of ionic radii used in these calculations are listed in Table 22.

7. Miscellaneous Reactions

a. $BrF_5 + AlF_3$

Material

AlF_3. Allied Chemical and Dye Corp., General Chemical Division

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Table 22

Values of Ionic Radii

		Reference
Cs^+	1.69 A	(26)
Mg^{++}	0.65	(26)
NO_2^+	1.75	*
F^-	1.36	(26)
BrF_6^-	2.66	*

* Calculated Values

Procedure

Aluminum fluoride (0.0741 mole) and bromine pentafluoride (0.902 mole) were placed in the nickel reactor and agitated for 16 hours at 100°C.

Results

The purpose of this investigation was to prepare an aluminum poly-halide, $Al(BrF_6)_3$. While this compound, as such, would not be a sufficiently energetic oxidizer to meet target specifications, it was expected that certain fundamental chemical characteristics might be learned to form the basis for other reactions leading to high energy oxidizers.

The postulated reaction in this work was:

$$6BrF_5 \rightleftharpoons 3BrF_4^+ + 3BrF_6^-$$

$$AlF_3 \rightleftharpoons Al^{+++} + 3F^-$$

$$AlF_3 + 6BrF_5 \xrightarrow{\quad 100°C. \quad} Al(BrF_6)_3\downarrow + 3BrF_5$$
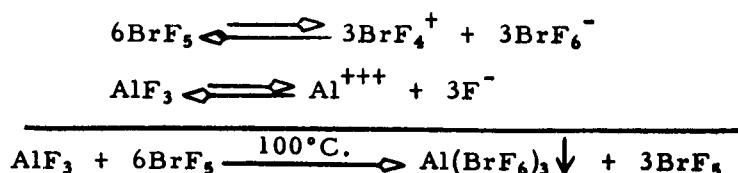
The results are shown in Table 7. Based on the weight increase of solid product recovered over the weight of starting AlF_3, a 15.9% conversion of AlF_3 to $Al(BrF_6)_3$ may have occurred. The product, a light tan solid, was an active oxidizing agent, igniting polyethylene film on contact and liberating iodine from aqueous solutions of potassium iodide.

The crude solid probably contained unreacted aluminum fluoride. Ideally, complete removal of the unreacted aluminum fluoride and sub-sequent analysis of the purified aluminum polyhalide is necessary for firm characterization of the reaction product. The reactive nature of the product limited the possible purification schemes that could be used. As a result, only limited data were obtained and that by inference.

Based on weight increase of the recovered solid, after removal of the volatile BrF_5, the following conversion of AlF_3 was calculated:

Wt. of AlF_3 added   =   6.22 g.

Theoretical wt. increase of solid for 100% conversion of AlF_3 to $Al(BrF_6)_3$ =   38.87 g.

Actual wt. increase of solid   =   6.16 g.

Calculated conversion of AlF_3 to $Al(BrF_6)_3$ =   15.85%

Based on bromine content of the recovered solid, the following conversion of AlF_3 was determined:

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Theoretical bromine content for 100% Al(BrF$_6$)$_3$ = 39.39 wt. %

Actual bromine content of solid = 41.6 wt. %

BrF$_5$ in solid (by wt. increase = 6.16 g.

AlF$_3$ in solid = 6.22 g.

Total solid recovered = 12.38 g.

Calc. bromine in solid $\dfrac{(6160)79.916}{174.916}$ = 2.81 g.

Actual bromine in solid (12.38)(.416) = 5.15 g.

Theoretical wt. increase of AlF$_3$ for 100%
conversion AlF$_3$ to Al(BrF$_6$)$_3$ = 38.87 g.

Theoretical bromine in 38.87 g. Al(BrF$_6$)$_3$ = 17.76 g.

Maximum conversion of AlF$_3$ to Al(BrF$_6$)$_3$
$\dfrac{5.15\,(100)}{17.76}$ = 29.0%

The maximum calculated conversion of AlF$_3$ to Al(BrF$_6$)$_3$ based on weight increase is 15.85%, but based on bromine content the maximum conversion is 29.0%. This discrepancy was not resolved. A possible error in bromine determination or the formation of Al(BrF$_4$)$_3$, rather than Al(BrF$_6$)$_3$, could explain this.

It can be concluded that a reaction occurred, but the product was not conclusively identified.

b. __BrF$_5$ + N$_2$O$_5$ + HF__

Material

HF. The Matheson Company, Inc. Anhydrous, Purity 99.0%

N$_2$O$_5$. Dinitrogen pentoxide was prepared by the method of Gruenhut, Goldfrank, Cushing and Ceasor (23) in a silent discharge apparatus. P$_2$O$_5$ was spread over the surface of frozen nitric acid in an oxygen atmosphere. The ozonizer was activated and the reactants were warmed to room temperature in an ozone atmosphere. After the initial reaction subsided, the reactants were stirred and heated to 40°C. for one hour. The ozone temperature was maintained for several additional hours. The product was collected as a white solid in a trap cooled to -78°C. The trap was warmed to 0°C. and flushed with nitrogen to remove the N$_2$O$_5$. The apparatus is shown in Figure 9.

Figure 9

Apparatus for Preparation of N_2O_5 and Reaction of N_2O_5
with Interhalogens
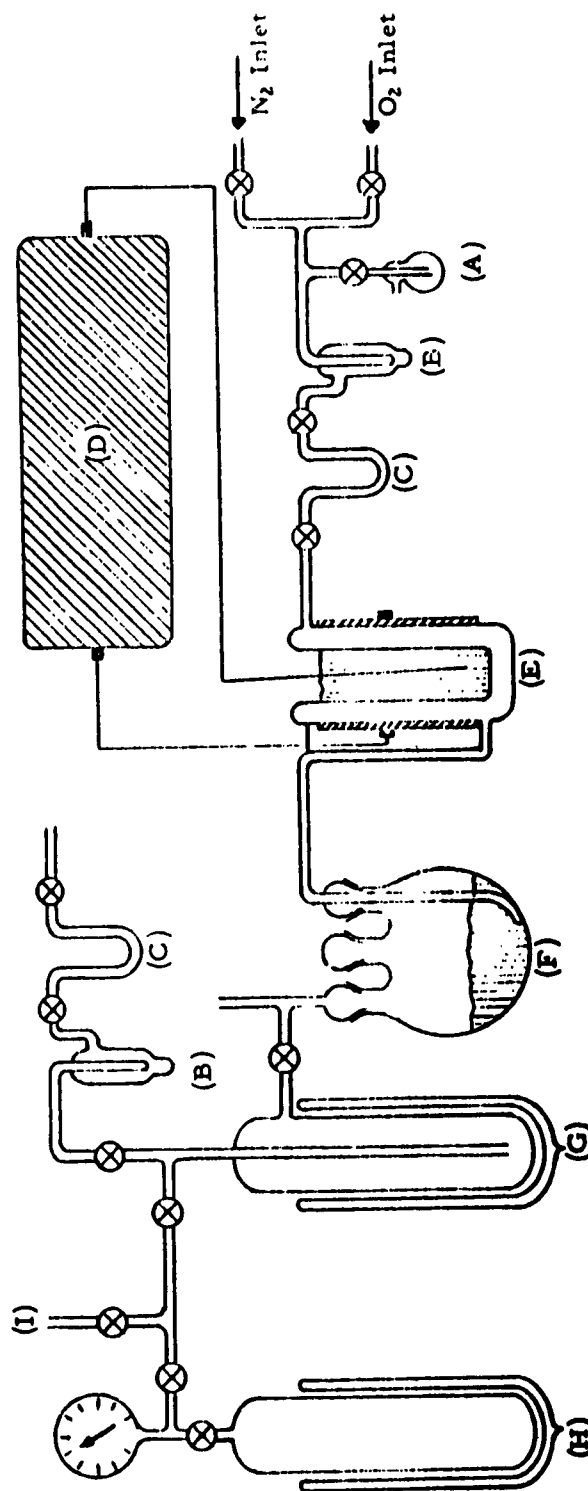
(A) Safety bubble-off
(B) Bubble-counters (conc H_2SO_4)
(C) Drying tubes (P_2O_5)
(D) Transformer (15,000 v. 30 ma.)
(E) Ozonizer

(F) Reactor for prepration of N_2O_5 (HNO_3 and P_2O_5)
(G) N_2O_5 collection trap (-78°C)
(H) Reactor for N_2O_5 and interhalogens
(I) Metal high vacuum line inlet

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Apparatus

The apparatus is described in Figure 9. The reactor was constructed of nickel.

Procedure

Hydrogen fluoride, dinitrogen pentoxide and bromine pentafluoride were condensed into the nickel reactor, Figure 9, at -196°C. The reactants were warmed to room temperature and allowed to stand for 16 hours. A maximum pressure of 80 psig was recorded in the reactor at room temperature. The reactor was shaken for several minutes and the products were fractionated and analyzed.

Results

The purpose of the selected solvent system was to promote the formation of NO_2BrF_6. It was speculated that the ionization of N_2O_5 in HF might occur as

$$N_2O_5 \underset{\Longleftarrow}{\overset{HF}{\Longrightarrow}} NO_2^+ + NO_3^-$$
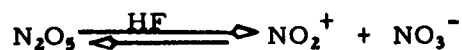
and subsequent reaction with bromine pentafluoride would occur as

$$NO_2^+ + NO_3^- + 2HF \longrightarrow (NO_2^+)(HF_2^-) + (H^+)(NO_3^-)$$

$$BrF_5 + (NO_2^+)(HF_2^-) \longrightarrow NO_2BrF_6 + HF$$
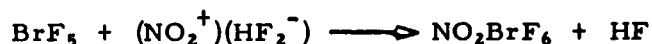
The last equation presupposes some ionization of bromine penta-fluoride as an acid in HF:

$$2HF + BrF_5 \longrightarrow H_2F^+ + BrF_6^-$$

$$(NO_2^+)(HF_2^-) + (H_2F^+)(BrF_6^-) \longrightarrow NO_2^+BrF_6^- + 3HF$$
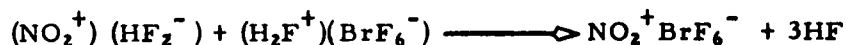
The ionization of a halogen fluoride as an acid in liquid hydrogen fluoride has, to our knowledge, never been reported.

It is considered unlikely that N_2O_5 might ionize in HF as

$$N_2O_5 \xrightarrow{\quad HF \quad} NO_2^- + NO_3^+$$

Depending upon the mode of ionization of both N_2O_5 and BrF_5 in hydrogen fluoride, there exists the possibility of four different compounds being formed.

A reaction occurred and the principal product was a reactive yellow liquid which gave a strong positive test with aqueous potassium iodide and ignited tissue paper on contact. The elemental composition was:

		Found	Theoretical for NO_2BrF_6
Wt%	N	5.2 ± 0.25	5.8
	F	61.6 ± 0.5	47.5
	Br	26.0 ± 0.8	33.3
	O	-	13.4
			100.0

The yellow liquid was calculated to have the empirical formula $NBrF_{9.6}X$, where X, an unknown, constitutes 7.2 weight per cent of the molecule. The data is most reasonably explained by assuming the the product is a nitryl hexafluorobromate-hydrogen fluoride complex with the formula $NO_2BrF_6 \cdot XHF$, where X is either 3 or 4. Ansley, Hetherington and Robinson (18) have reported addition of nitryl fluoride to bromine trifluoride to result in a yellow viscous liquid. Their material was believed to contain (NO_2BrF_4) although no solid product could be recovered. The yellow color was, according Aynsley, due to the nitronium ion NO^+_2. Certainly the same reasoning may be applied to the product isolated in this work.

The vapor pressure of the liquid product was measured over the temperature range 0° to 65°C. (see Table 21).

In Figure 10, a plot of log P_{mm} versus the reciprocal absolute temperature is given. The appropriate constants for the equation

$$\log P_{mm} = \frac{A}{T^\circ K} + B$$

are: A = -1837 and B = 8.311. From this equation the calculated boiling point of the liquid is 65.1°C. In Figure 10 the relative errors in pressure gauge readings are shown as vertical lines through the experimental points.

From the above Clausius-Clapeyron Equation, the calculated molar heat of vaporization, ΔH_v, is 8.40 kcal. mole^{-1}, whereas the Trouton's constant $\dfrac{\Delta H_v}{T_b}$, is 24.8 cal. deg.$^{-1}$mole^{-1}.

It is of interest to compare the value of Trouton's constant calculated for the above liquid, 24.8 cal. degree^{-1}mole^{-1}, with that of anhydrous hydrogen fluoride, 6.1 cal. degree^{-1}mole^{-1} (25). It would thus appear likely that if hydrogen fluoride were present in the liquid product it would be complexed in some manner. Trouton's constant for a non-associated liquid is approximately 21 cal. degree^{-1}mole. Higher values are usually indicative of some type of association between molecules in the liquid phase.

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Table 21

Vapor Pressure, Temperature Data on Liquid Product From N_2O_5 - HF - BrF_5 Reaction

Temperature		Pressure	
°C.	°K.	Inches	mm.
0	273	1.6	40
18	291	4.0	101
38	311	10.2	258
45	318	13.7	346
50	323	16.9	427
55	328	20.1	509
60	333	25.2	637
65	338	29.5	757

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Figure 10

Log p_{mm} versus $\frac{1}{T}$ for Liquid Product from Experiment 1740D-95

Temp. Range = 273-338° K.

$$\log p_{mm} = \frac{-1837}{T} + 8.311$$

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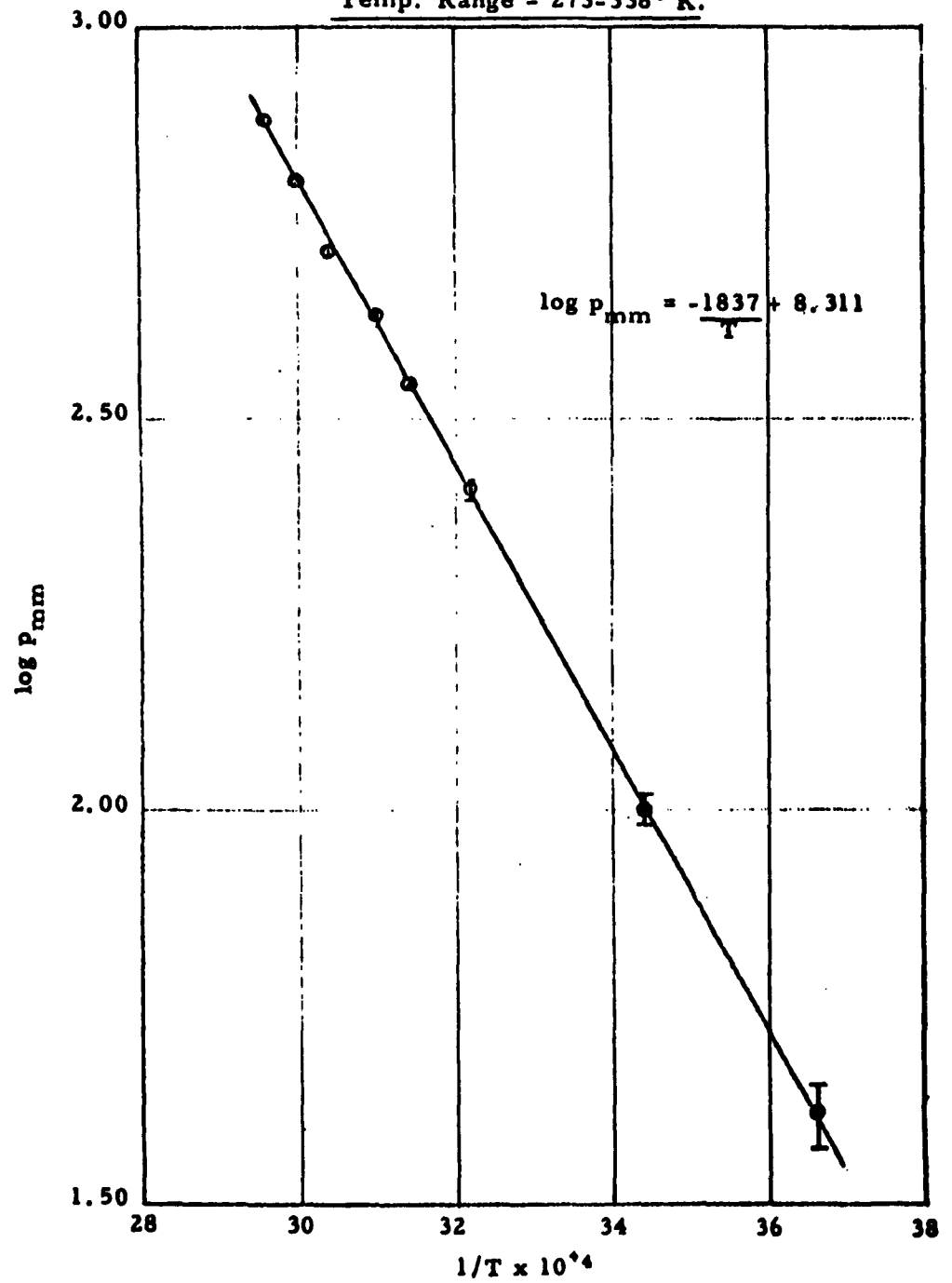
c. BrF_5 + AlF_3 + NOF

Material

AlF_3. Allied Chemical and Dye Corp., General Chemical Division.

NOF. Nitrosyl fluoride was prepared by the method of Brauer[13] by the reaction of fluorine with nitric oxide.

Procedure

In a typical experiment aluminum fluoride (0.0496 mole), nitrosyl fluoride (0.232 mole) and bromine pentafluoride (0.589 mole) were placed in the nickel reactor, warmed from -196°C. to 25°C. and permitted to stand for 72 hours at 25°C. with periodic agitation.

Results

The experiments listed in Table 11 were designed to increase the solubility of aluminum fluoride in halogen fluorides through the formation of nitrosyl complexes. Once increased solubility of the metal fluoride had been achieved it was expected that solvolysis leading to polyhalide formation might follow. Partial success through this approach was realized. For example, the results of experiment 1876D-13, Table 11, may be explained by the assumption that nitrosyl fluoride reacted with the aluminum fluoride forming an addition compound

$$NOF + AlF_3 \longrightarrow NO^+ \left[AlF_4^-\right]$$
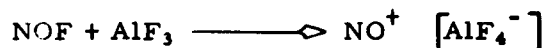
with the reacted nitrosyl fluoride possibly combining with bromine pentafluoride (present in the system in large excess) to form nitrosyl hexafluorobromate

$$NOF + BrF_5 \longrightarrow NO^+ \left[BrF_6^-\right]$$

No nitrosyl salts of fluoro-aluminum complexes have been reported in the literature although the addition compound $NO^+AlClF_4^-$ is known and had been studied extensively [24]. Nitrosyl hexafluorobromate ($NO^+BrF_6^-$) ordinarily either is not formed by the reaction of NOF with BrF_5 or it is unstable at 25°C. and decomposes to the initial reactants. In this work the possibility exists that $NOBrF_6$ was formed and stabilized by the $NOF-AlF_3$ complex.

On the basis of this work it can be tentatively concluded that the solvolysis of aluminum fluoride in a mixture of nitrosyl fluoride and bromine pentafluoride results in the formation of a solid containing bromine, fluorine, and nitrogen. This product is assumed to be either a mixture of nitrosyl tetrafluoroaluminate and nitrosyl hexafluorobromate ($NOAlF_4$ + $BOBrF_6$) or impure nitrosyl aluminum tetrakis hexafluorobromate (V) $\left[NOAl(BrF_6^-)4\right]$.

Section II: Reactions with Tetrafluorochlorates

A. Reactions with Metal Tetrafluorochlorate (ClF_4) Compounds

1. Objective

While the success achieved in the preparation of the new compounds $Rb^+ClF_4^-$, $Cs^+ClF_4^-$ and $K^+ClF_4^-$ did not provide a fluorine containing product that met the target impulse specifications, it was hoped that these compounds could be utilized in metathesis reactions that would yield high energy solid oxidizers such as NO_2ClF_4. Such compounds cannot be prepared by more direct methods. Further, if these exchange reactions were successful this would provide more evidence of the ionic structure of the $MClF_4$ compounds. It would establish whether the structures are simple complexes $MF \cdot ClF_3$ or the ionic form $M^+ClF_4^-$.

Postulated metathesis reactions, with chlorine trifluoride as solvent, are:

(a) $3Cs^+ ClF_4^- + Al^{+++} + 3F^- \xrightarrow{ClF_3} Al(ClF_4)_3 + 3CsF$

(b) $Rb^+ ClF_4^- + NO_2^+ SbF_6^- \xrightarrow{ClF_3} NO_2^+ ClF_4^- + Rb^+ SbF_6^-$

(c) $Rb^+ ClF_4^- + NO_2^+ BF_4^- \xrightarrow{ClF_3} NO_2^+ ClF_4^- + Rb^+ BF_4^-$
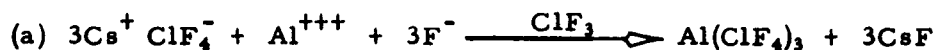
A novel reaction scheme designed to produce NF_2ClF_4 by the reaction of ultraviolet irradiated tetrafluorohydrazine with cesium tetrafluorochlorate was also investigated.

2. Reactions with $MClF_4$ Compounds
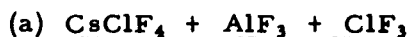
(a) $CsClF_4 + AlF_3 + ClF_3$

Material

AlF_3. Allied Chemical and Dye Corporation, General Chemicals Division.

ClF_3. The Matheson Company, Inc.

$CsClF_4$. Prepared by the reaction of $CsF + ClF_3$ at 100°C. as described in Section IA, 2e. Analysis of the product showed:

		Found	Theoretical for $CsClF_4$
Wt. %	Cl	13.3, 13.4	14.5
	F	30.1, 30.2	31.1

Apparatus

The general purpose metal high vacuum line used in this work is described in Figure 1. The nickel reactor is described in Figure 2.

Procedure

In a typical experiment $CsClF_4$(0.026 mole) AlF_3 (0.075 mole) and ClF_3(0.671 mole) were placed in the nickel reactor. The reactor was then closed, placed on a mechanical agitator (Burrell Shaker) and the reactants were agitated for 24 hours at 100°C. The product was then fractionated and analyzed.

Results

Multivalent tetrafluorochlorate salts such as $Al(ClF_4)_3$ cannot be prepared by the direct solvolysis of aluminum fluoride in chlorine trifluoride. It was hoped that this compound could be prepared by some indirect route, possibly by the following reaction scheme:

(a) $3CsClF_4 + AlF_3 \xrightarrow{\quad ClF_3 \quad} 3CsF + Al(ClF_4)_3$

An alternate course for the reaction is:

(b) $CsAlF_4 + AlF_3 \xrightarrow{\quad ClF_3 \quad} CsAl(ClF_4)_3$

In reaction (a) the chlorine trifluoride would act as an inert solvent merely providing a medium for dissolution of the reactions followed by normal separation into ions. In reaction (b) proposed self-ionization of the chlorine trifluoride would enable it to take part in the reaction as well as provide a solvent medium. An excess of chlorine trifluoride was used to provide a possible driving force for the reaction.

The results of several experiments are shown in Tables 9 and 23. In all cases the weight of solid product recovered at the end of the experiment was less than the combined weights of the starting solids AlF_3 and $CsClF_4$. If the predicted reaction (a) had occurred or if there was no reaction, there would be no change in weight of solid product. If reaction (b) had taken place, an increase in weight of solid would have resulted.

The loss in weight of solid product observed over the starting solid was attributed to the decomposition of $CsClF_4$ to CsF and ClF_3. There was no evidence for the presence of $Al(ClF_4)_3$ in the final product.

(b) $\underline{RbClF_4 + NO_2SbF_6 + ClF_3}$
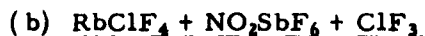
Material

ClF_3. The Matheson Company, Inc.

NO_2SbF_6. Prepared by the following reaction:

$$BrF_2{}^+ SbF_6{}^- + N_2O_4 \xrightarrow{\quad 25°C. \quad} NO_2SbF_6\downarrow + \text{volatile products}$$

The salt was heated in vacuum to 70°C. to remove absorbed volatile products.

$RbClF_4$. Prepared by the reaction of $RbF + ClF_3$ as described in Section IA, 2d.

Table 23

Metathesis Reactions in Solvent System

Exp. No.	Reactants and Solvent					Molar Ratio A/B/C	Weight increase (g) of Product over Reactant	Results
	A	moles B	moles C	moles			
1909D-77	CoClF$_4$	0.20 AlF$_3$	0.095 ClF$_3$	0.71	1/0.28/3.6	-8.38 over CoClF$_4$ and AlF$_3$	No Al(ClF$_4$)$_3$ was not produced as a stable product; 45% of CoClF$_3$ decomposed to CoF
1909D-82	Mg(BF$_4$)$_2$	0.086 NOClF$_4$	0.16 ClF$_3$	0.79	1/2.8/12.7	+9.63 over Mg(BF$_4$)$_2$	Mg(ClF$_4$)$_2$ was not produced as a stable product; chemical analysis SCl = 0.0, %F = 61.2, %B = 7.1 %H = 10.1 Analysis indicates possibly Mg(BF$_4$)$_2$ · NOF or 2.5 NOBF$_4$ + MgF$_2$
1909D-86	Mg(ClO$_4$)$_2$	0.086 NOClF$_4$	0.075 HF	1.97	1/4.2/104	-0.783 over Mg(ClO$_4$)$_2$	Mg(ClF$_4$)$_2$ was not produced as a stable product; chemical analysis SCl = 0.0, %F = 59.5, %H = 7.4 Analysis indicates possibly NO$_2$F · MgF$_2$ · 3HF
1909D-89	MgF$_2$	0.082 NOClF$_4$	0.22 HSO$_3$F	0.256	1/2.6/3.13	+4.822 over MgF$_2$	Mg(ClF$_4$)$_2$ was not produced as a stable product; chemical analysis %F = 29.1, %H = 8.47
1909D-91							%S = 18.7, %Cl = 0:1 Analysis indicates possibly 0.42 moles MgF$_2$ + 0.58 moles NOSO$_3$F

Apparatus

The reactor is shown in Figure 11. This Vycor reactor was attached to a typical metal high vacuum line for manipulating volatile products or reactants.

Procedure

Weighed amounts of rubidium tetrafluorochlorate and nitronium hexafluorrantimonate are charged into the reactor under a nitrogen atmosphere. The reactor is then attached to the vacuum system, evacuated and cooled to -78°C. A predetermined amount of chlorine trifluoride is condensed onto the salts, the mixture warmed to -63°C. to effect melting and then brought to the desired reaction temperature. The chlorine trifluoride solution remains liquid at temperatures as low as -78°C. The reactor is manually agitated intermittently for a two-hour period to insure proper mixing. Samples of the vapor above the solution are removed for infrared examination and the mixture is then vacuum distilled at the reaction temperature until the over-head vapor pressure is less than the pressure due to ClF_3(0.4 inches abso-lute at -63°C.). When the reaction and distillation are conducted at -63°C. or lower, a small quantity of a less volatile component remains behind in addition to the nonvolatile salt products. Characterizations of the volatile chlorine trifluoride fraction, the less volatile component and the salt are made by infrared and elemental analyses.

Results

The purpose of this work was to prepare NO_2ClF_4 by the following metathesis reaction:

$$RbClF_4 + NO_2SbF_6 \xrightarrow[-23°C.]{ClF_3} NO_2ClF_4 + RbSbF_6$$
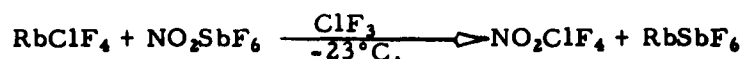
If the predicted compound NO_2ClF_4 formed but decomposed, it was expected to decompose as follows:

$$NO_2ClF_4 \longrightarrow NO_2F + ClF_3$$

Earlier attempts to prepare NO_2ClF_4 by the reaction of NO_2F with ClF_3 (Section 1A, 5b) were unsuccessful apparently due to thermal instability of the structure. In this attempt the primary objective was to prepare and isolate the compound NO_2ClF_4. If the compound could not be isolated then it was our intention to determine the conditions that resulted in decomposition and to identify the decomposition products.

The results of several experiments are shown in Table 24. If the reaction occurred as shown above and the NO_2ClF_4 decomposed to volatile products, complete removal of volatile products should leave only the stable salt $RbSbF_6$. Further, the loss in weight of the recovered solid over the weight of starting solid reactants should correspond to the theoretical weight loss if NO_2ClF_4 did form but decomposed. This was shown to be the case. Theoretical weight losses for the formation and decomposition of NO_2ClF_4 were observed and the stable solid recovered showed no nitrogen on analysis, as expected for $RbSbF_6$. The volatile products were identified as NO_2F and ClF_3 by infrared.

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Figure 11

Vycor Reactor for Interhalogen Studies

4 mm. glass stopcock

24/40 Standard Taper
Fitting

4"

25 mm.

1/2" Teflon-coated
Stirring Bar

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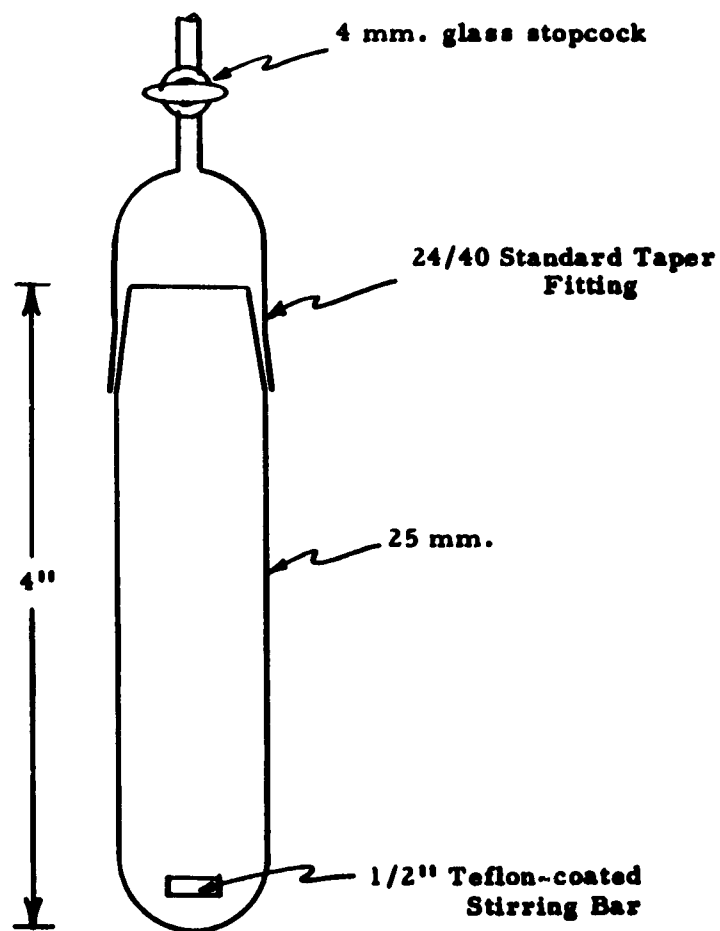
Table 24

Reaction of NO₂SbF₆ with RbClF₄

Exp. No.	NO₂SbF₆ wt.(g.)	NO₂SbF₆ m.mole	RbClF₄-0.16RbF wt(g.)	RbClF₄-0.16RbF m.moles	ClF₃ (ml.)	Reaction Temp. °C.	Reactor	Solid Product Analysis %N₂	Product Weight loss g.	theor. NO₂ClF₄ g.	theor. weight loss
1691-14	0.739	2.62	0.570	2.67	3.0	0.0	Vycor	0.0	0.485	0.438	90
-21	0.241	0.85	0.246	1.16	4.8	-23	30 ml SS (Prefluorinated)	0.0	0.126	0.135	94
-24	0.368	1.30	0.552	2.59	6.4	-46	"	—	0.200	0.206	97
-27	0.512	1.82	0.363	1.71	6.3	-63	"	1.49	0.265	0.286	93
-29	0.593	2.10	0.879	4.12	no solvent	25-27	Vycor	—	0.131[a]	0.331	b
-33	0.44		0.63		3.2	-23	30 ml.SS	0	I.R. absorptions, BaF₂ cell 5.6, 5.8, 6.2, 7.7, 9.0. NO₂F		

[a] After 12 hours of vacuum distillation at 25°C.

b Attack of Vycor when solids treated with ClF₃ at end of experiment.

When the reaction was conducted at a temperature of -63°C. or lower, and the chlorine trifluoride solvent was removed at this temperature, a small amount of a less volatile product was observed to remain behind. Attempts to characterize this material by infrared, mass spectrometry, and molecular weight showed that it was not the sought for NO_2ClF_4. Although the ClF_3 used was at least 99% pure, there was the possibility that traces of chlorine oxides were present and may have been responsible for this observation.

On the basis of the results which have been obtained it appears that NO_2ClF_4 does form from $RbClF_4$ and NO_2SbF_6 in ClF_3 and decomposes at temperatures as low as -63°C. to produce ClF_3 and NO_2F. Although it is possible that the nitronium hexafluorantimonate is fluorinated by the rubidium tetrafluorochlorate to produce nitryl fluoride directly, this route is improbable

$$RbClF_4 + NO_2SbF_6 \longrightarrow\!\!\!\!\!/ NO_2F + RbSbF_6 + ClF_3$$

The nitronium salt is insoluble in ClF_3 but compatible and can be recovered unchanged when stirred with ClF_3. It is extremely doubtful that the relatively weak fluorinating agent, $RbClF_4$, would fluorinate the nitronium salt when the powerful fluorinating agent, ClF_3, is inactive. It therefore appears necessary to propose that a metathesis reaction occurs leading to the precipitation of $RbSbF_6$ and the transitory NO_2ClF_4 which then decomposes further to NO_2F and ClF_3.

(c) $CsClF_4 + N_2F_4$

Material

N_2F_4. E. I. Dupont de Nemours, purity 99% +

$CsClF_4$. $CsClF_4$ was prepared by the reaction of:

$$CsF + ClF_3 \longrightarrow CsClF_4$$

as described in Section IA, 2e. The cesium fluoride as received from the British Drug House, Ltd. was dried under vacuum at 100-100°C. for 16 hours and then reacted with excess ClF_3. Analysis of the solid product indicated that it contained large amounts of unreacted cesium fluoride coordinated with hydrogen fluoride.

		Found	Theoretical for 56% $CsClF_4$ 44% $CsF \cdot HF$	Theoretical for $CsClF_4$
W%	F	29.6	27.2	31.5
	Cl	8.14	8.14	14.5

Apparatus

The apparatus is shown in Figure 12. Careful design of the reactor system was considered extremely important. Possible side reactions of N_2F_4 with glass were eliminated by using only Teflon and calcium fluoride for the reactor and polypropylene, copper, and stainless steel components in the construction of the system. The distance between the irradiation area and the surface of the salt was made as short as possible to minimize

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Figure 12

Irradiation of N_2F_4

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$N_2F_4 \longrightarrow NF_2 \cdot \xrightarrow{U.V.} NF_2^* \longrightarrow NF \cdot + F \cdot$

$F \cdot + MClO_4 \longrightarrow MF + ClO_4 \cdot$

$NF_2 \cdot + ClO_4 \cdot \longrightarrow NF_2ClO_4$
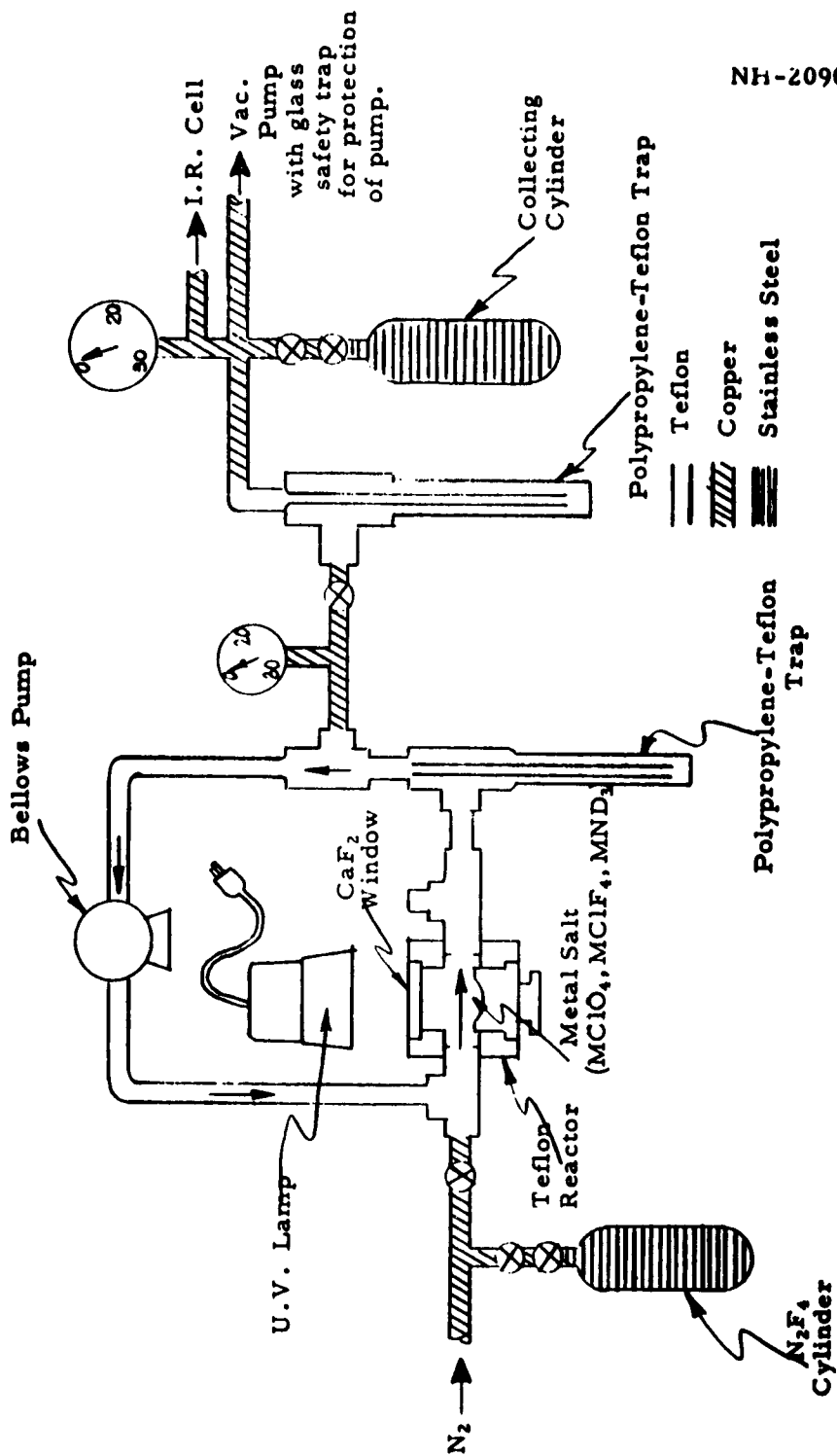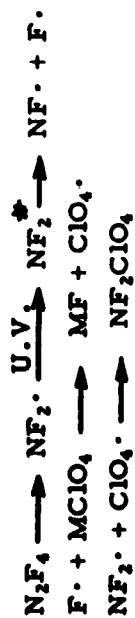
System contains no glass components and is comprised of Teflon, Polypropylene, Poly-Flo, Copper and Stainless Steel parts.

recombination reactions. The effectiveness of the system was further increased by using a continuous flow system permitting short residence times. Condensing traps were included as part of the recycle system to allow for rapid low temperature quenching of any gaseous products.

A Hanovia No. 30600 ultra violet lamp (1849-4000A°) was used to activate the tetrafluorohydrazine.

Procedure

In a typical experiment dried cesium tetrafluorochlorate was placed in the reactor cavity and the reactor system was sealed and evacuated. A weighed quantity of N_2F_4 was then admitted to the evacuated system to a pressure about 400 mm. The recycle trap was cooled with dry ice, the bellows pump was turned on and the reactants were irradiated for a period of 3-4 hours. The gaseous products were then collected in a low temperature trap (-196°C.) and the solid and volatile products were weighed and analyzed.

Results

Previous work in our laboratory on the irradiation of tetrafluoro-hydrazine alone with ultraviolet light (1849A°-2100°A) in a glass-free apparatus showed that the decomposition products were nitrogen trifluoride and nitrogen. The decomposition is considered to take place via the formation of fluorine atoms:

$$NF_2-NF_2 \rightleftharpoons 2NF_2\cdot$$

$$NF_2\cdot \xrightarrow{U.V} NF\cdot + F\cdot$$

$$NF\cdot + NF_2\cdot \longrightarrow NF_3 + 1/2 N_2$$

$$F\cdot + NF_2\cdot \longrightarrow NF_3$$
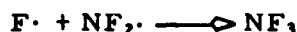
In this study the intent was to activate NF_2 radicals in the presence of cesium tetrafluorochlorate as a possible route to the formation of NF_2ClF_4. The fluorine atoms which form were expected to react and produce transitory intermediates capable of coupling with NF_2 radicals present in large excess.

$$NF_2\cdot \xrightarrow{U.V} NF\cdot + F\cdot$$

$$F\cdot + CsClF_4 \longrightarrow CsF + ClF_4\cdot$$

$$NF_2\cdot + ClF_4\cdot \longrightarrow NF_2ClF_4$$
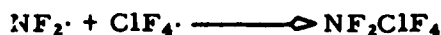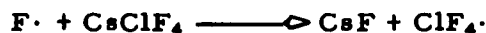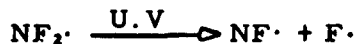
Fluorine is known to react in a similar manner with potassium chlorate to form Cl_2O_6, as described by Bode and Klesper (29)

$$F_2{(g)} + KClO_3{(s)} \xrightarrow{-50°C.} 2KF + Cl_2O_6$$
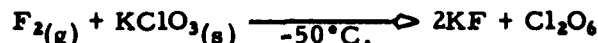
where the liberation and subsequent dimerization of ClO_3 radicals was postulated.

No reaction was observed in a series of three experiments with $CsClF_4$

and N_2F_4. Initially the reaction was conducted in the absence of irradiation and no apparent change in the salt or the N_2F_4 was observed. In two attempts at irradiation, the salt became somewhat pasty and changed in color to a yellow-orange in contrast to the starting rose-red. However, no significant decomposition of the N_2F_4 had resulted and infrared examination of the solid indicated no change. The inertness of the N_2F_4 had been observed in earlier irradiation experiments but the situation had become "normal" again on repeated attempts. Surprisingly, it was not possible to cause N_2F_4 to decompose appreciably to NF_3 after this latest failure. Several experiments were conducted with pure N_2F_4 without success and the entire system was checked over several times without finding the difficulty. New ultraviolet lamps as well as bulbs were substituted without success. Materials such as air or water were added to determine whether the presence of unknown impurities may have acted as catalysts in the earlier irradiation studies, but NF_3 did not form in any of these cases.

In view of the uncertainty regarding the activation of the tetrafluorohydrazine, which was considered to be a vital part of the reaction process, no conclusions can be made on the theoretical aspects of this approach to the synthesis of NF_2ClF_4.

(d) $RbClF_4 + NO_2BF_4 + ClF_3$

Material

NO_2BF_4. Nitronium tetrafluoroborate was prepared by the reaction of dinitrogen tetroxide and boron trifluoride in bromine trifluoride in a Monel reactor at 25°C. The volatile components were removed in vacuo at 50°C. The solid nitronium salt was removed from the reactor in a dry box and stored under anhydrous conditions.

$RbClF_4$. Prepared as described previously.

Apparatus

The Vycor reactor is described in Figure 11.

Procedure

Nitronium tetrafluoroborate (0.39 g.) and $RbClF_4 \cdot 0.16 \, RbF$ (1.1 g.) were added to the reactor, the reactor evacuated and 2.0 ml. of ClF_3 condensed on to the solid at -78°C. The reactor was warmed to 0°C. and maintained at this temperature for 0.5 hour and stirred with a magnetic stirrer. The product was then fractionated and analyzed.

Results

The objective here was to prepare and isolate the compound NO_2ClF_4:

$$Rb^+ClF_4^- + NO_2^+BF_4 \xrightarrow[\text{0°C.}]{\text{ClF}_3} NO_2^+ClF_4^- + Rb^+BF_4^-$$
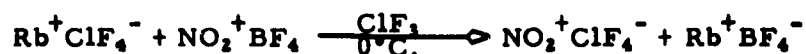
A reaction occurred at 0°C. and the volatile components were collected and weighed. The recovered solid weighed 0.28 g. less than the original solid

reactants. Apparently the reaction generated a volatile product rather than stable solid products. If the reaction proceeded in the expected manner and NO_2ClF_4 was formed but decomposed to volatile products, a 62 per cent conversion could be calculated on the basis of weight loss of solid reactants. Attempts to gain additional information on the presence of NO_2ClF_4 or its decomposition products were unsuccessful due to the large amount of ClF_3 present and the reactivity of the volatile product.

The observations are in general agreement with the work described in Section IA, 5b, which showed that NO_2ClF_4 could not be prepared by the solvolysis reaction of NO_2F and ClF_3. The metathesis reaction of $RbClF_4$ and NO_2SbF_6 in ClF_3 (Section IIA, 1b) apparently resulted in the formation and decomposition of NO_2ClF_4 at temperatures as low as -63°C.

B. Reactions with NOClF₄

1. Objective

The new compound nitrosyl tetrafluorochlorate ($NOClF_4$) was prepared by the solvolysis of nitrosyl fluoride in chlorine trifluoride (Section I5, 2a). Unfortunately this compound decomposes at approximately -5°C. to nitrosyl fluoride and chlorine trifluoride and, therefore, cannot be used in solid propellent formulations.

Studies then were pursued to use nitrosyl tetrafluorochlorate as an intermediate in the preparation of new multivalent polyhalides such as $Al(ClF_4)_3$, $Mg(ClF_4)_3$ and NO_2ClF_4. It was hoped that nitrosyl tetrafluorochlorate would undergo exchange reactions in solvent systems. If such reactions occurred, they would also provide more data on the structure of $NOClF_4$.

Another objective of this study was to investigate methods of stabilizing nitrosyl tetrafluorochlorate by the formation of adducts with high energy molecules.

(a) NOClF₄ + Mg(BF₄)₂ + ClF₃

Material

$Mg(BF_4)_2$. Magnesium tetrafluoroborate was prepared by the following reaction:

$$MgF_2 + BF_3 \xrightarrow[25°C.]{HF} Mg(BF_4)_2 + HF$$
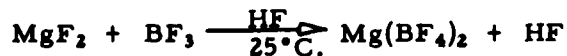
$NOClO_4$. Nitrosyl tetrafluorochlorate was prepared as described in Section IA, 5a.

ClF_3. The Matheson Company, Inc.

Apparatus

The general purpose metal high vacuum line is described in Figure 1 and the nickel reactor is shown in Figure 2.

Procedure

Magnesium tetrafluoroborate (0.056 mole), nitrosyl tetrafluoro--chlorate (0.16 mole) and chlorine trifluoride (0.70 mole) were placed in the nickel reactor and agitated (Burwell Shaker) for 16 hours at 25°C. The product was then fractionated and analyzed.

Results

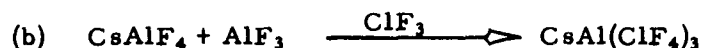Nitrosyl fluoroborate, $NOBF_4$, is a very stable compound (30) and its formation in a metathesis reaction would provide a driving force needed to form a less stable compound in the same reaction. On this reasoning the following reaction was predicted:

$$Mg(BF_4)_2 + NOClF_4 \xrightarrow{ClF_3} Mg(ClF_4)_2 + NOBF_4.$$
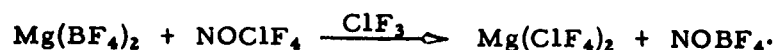
A reaction evidently occurred since the amount of solid product recovered at the end of the experiment was greater than the weight of the starting solid $Mg(BF_4)_2$. Analysis of the solid, however, did not support the presence of the desired product $Mg(ClF_4)_2$:

		Found	Theoretical for $Mg(ClF_4)_2$	Theoretical for $Mg(BF_4)_2 \cdot 3NOF$	Theoretical for $2.5NOBF_4 \cdot MgF_2$
Wt%	F	61.2	61.48	60.59	64.34
	Cl	0.0	28.68	0.00	0.00
	N	10.1	0.00	12.18	9.88
	B	7.1	0.00	6.27	7.63
	Mg		9.84	7.05	6.86
	O		0.00	13.91	11.29
			100.00	100.00	100.00

The results are listed in Table 23, Experiment 1089D-82

A complex reaction apparently occurred that did not produce $Mg(ClF_4)_2$, at least not to any significant extent. If the reaction involved decomposition of $NOClF_4$ to NOF and ClF_3 with the liberated NOF in turn complexing with $Mg(BF_4)_2$, i.e.:

$$3NOClF_4 + Mg(BF_4)_2 \longrightarrow Mg(BF_4)_2 \cdot 3NOF + 3ClF_3$$

a weight gain of solid over the weight of $Mg(BF_4)_2$ initially added would have resulted. An alternate possibility is based on the assumption that the predicted reaction occurred followed by decomposition of $Mg(ClF_4)_2$ to magnesium fluoride,

$$Mg(BF_4)_2 + 2NOClF_4 \xrightarrow{ClF_3} Mg(ClF_4)_2 + 2NOBF_4 + ClF_3$$

$$Mg(ClF_4)_2 \longrightarrow MgF_2 + ClF_3$$

$$\overline{Mg(BF_4)_2 + 2NOClF_4 \longrightarrow 2NOBF_4 + 3ClF_3 + MgF_2}$$
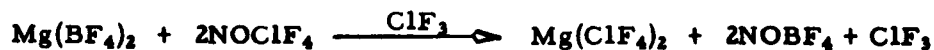
This would indicate that $Mg(ClF_4)_2$ is unstable and decomposes to MgF_2 and

ClF_3. The direct solvolysis of MgF_2 in ClF_3 (Section 1A, 3a) also showed that either a reaction did not occur or the desired product $Mg(ClF_4)_2$ formed but decomposed to the starting reagents.

(b) $NOClF_4$ + N_2F_4

Material

N_2F_4. Prepared by the reaction of NF_3 + Copper at 500°C. The N_2F_4 was purified by low temperature fractionation.

$NOClF_4$. Prepared as previously described.

Apparatus

The same as that used in the previous experiment.

Procedure

Nitrosyl tetrafluorochlorate (0.072 mole) and tetrafluorohydrazine (0.08 mole) were added to the reactor and allowed to stand at 25°C. for 16 hours. The product was then fractionated and analyzed.

Results

It had been reported that tetrafluorohydrazine and nitrosyl chloride reacted to form a solid product at low temperatures (31). Although the structure of this adduct was not known it was considered worthwhile to investigate the possibility of stabilizing $NOClF_4$ by complexing with N_2F_4, i.e.:
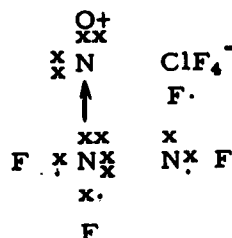
There was no evidence of reaction of the N_2F_4 with $NOClF_4$ or of any complex formation over the temperature range -79°C. to 25°C. All of the tetrafluorohydrazine was recovered. The experimental conditions and results are listed in Table 8, Experiment 1876D-45.

(c) $NOClF_4$ + $Mg(ClO_4)_2$ + HF

Material

$NOClF_4$. Prepared as described.

$Mg(ClO_4)_2$. The Fisher Scientfic Company, Anhydrous.

HF. The Matheson Company, Inc. , Anhydrous.

Apparatus

The same as used previously .

Procedure

Nitrosyl tetrafluorochlorate (0.075 mole), magnesium perchlorate (0.018 mole) and anhydrous hydrogen fluoride (1.97 mole) were placed in the reactor and agitated at 25°C. for 24 hours. The products were then fractionated and analyzed.

Results

In experiment 1089D-86, Table 23, hydrogen fluoride was used as the solvent medium for the following postulated reaction:

$$Mg(ClO_4)_2 + 2NOClF_4 \xrightarrow{\text{HF}} Mg(ClF_4)_2 + 2NOClO_4$$
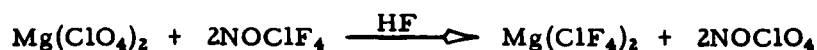
In this reaction the formation of $NOClO_4$, a known stable salt (32) was expected to force the reaction as indicated but analysis of the recovered solid product did not support the presence of $Mg(ClF_4)_2$ in the crude solid.

		Found	Theoretical for $Mg(ClF_4)_2$	Theoretical for $NO_2F \cdot MgF_2 \cdot 3HF$
Wt. %	Cl	0.0	28.68	0.00
	F	59.5	61.48	60.85
	N	7.4	0.00	7.47
	Mg	-	9.84	12.98
	H	-	0.00	1.61
	O	-	0.00	17.09
			100.00	100.00

The analysis generally supported a complex product, possibly a mixture of NO_2F, MgF_2 and HF. Since hydrogen fluoride forms complexes with metal fluorides, it did not serve as a useful solvent in any of the solvolysis reactions.

(d) NOClF₄ + MgF₂ + HSO₃F

Material

NOClF₄. Prepared as described.

MgF₂. The Matheson Company, Inc., Matheson, Coleman and Bell Division.

HSO₃F. Allied Chemical and Dye Corporation, General Chemicals Division.

Apparatus

The same as used in the above experiments.

Procedure

Nitrosyl tetrafluorochlorate (0.212 mole) magnesium fluoride (0.082 mole) and fluorosulfonic acid (0.256 mole ·) were placed in the reactor and agitated for 24 hours at 25°C. The product was then fractionated and analyzed.

Results

Fluorosulfonic acid was used as a solvent in Experiment 1089D-89, Table 23, for the metathesis reaction with magnesium fluoride and nitrosyl tetrafluorochlorate. The expected reaction was:

$$MgF_2 + 2HSO_3F \longrightarrow Mg^{++} + 2SO_3F^- + 2HF$$
$$2NOClF_4 \longrightarrow 2NO^+ + 2ClF_4^-$$

$$MgF_2 + 2HSO_3F + 2NOClF_4 \longrightarrow Mg(ClF_4)_2 + 2NOSO_3F + 2HF$$
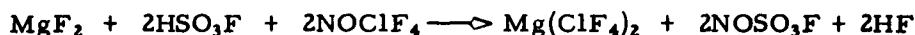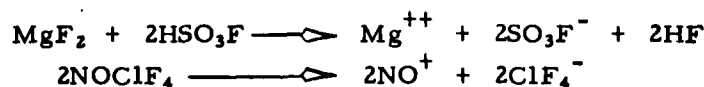
In this case the magnesium fluoride would be acting as a base, producing magnesium fluorosulfonate which could react in a metathesis reaction with nitrosyl tetrafluorochlorate.

A reaction occurred in this system but analysis of the solid product indicated that chlorine was not present to any significant extent. This analysis also showed that the desired product $Mg(ClF_4)_2$ was not present in the crude solid recovered.

		Found	Theoretical for $Mg(ClF_4)_2$	Theoretical for $0:41 MgF_2 + 0.58 NOSO_3F$
Wt%	Cl	0.0	28.68	0.00
	F	29.1	61.48	26.49
	N	8.5	0.00	8.09
	O	-	0.00	36.97
	S	18.7	0.00	18.52
	Mg	-	9.84	9.93
			100.00	100.00

The analysis corresponds to a mixture of magnesium fluoride and nitrosyl fluorosulfonate which could have resulted from the following reaction

$$NOClF_4 + HSO_3F \longrightarrow NOSO_3F + HF + ClF_3$$

with the magnesium fluoride not even entering the reaction, possibly due to insolubility in the fluorosulfonic acid.

(e) NOClF_4 + N_2O_4

Material

NOClF_4. Prepared as described.

N_2O_4. The Matheson Company, Inc.

Apparatus

The same as above.

Procedure

Nitrosyl tetrafluorochlorate (0.049 mole) and dinitrogen tetroxide (0.329 mole) were placed in the reactor and agitated for several hours at 25°C. The product was then distilled into a Pyrex glass trap, fractionated and analyzed.

Results

This work was of an exploratory nature designed primarily to determine if any reaction would occur between nitrosyl tetrafluorochlorate and dinitrogen tetroxide, such as:

a) $NOClF_4 \rightleftharpoons NOF + ClF_3$

$N_2O_4 + NOF + ClF_3 \longrightarrow Cl(NO_2)_3 + NO_2 + NOF$

or

b) $NOClF_4 + N_2O_4 \longrightarrow NO_2ClF_4 + N_2O_5$

or

c) $2NOClF_4 \rightleftharpoons 2NOF + 2ClF_3$

$3N_2O_4 + 2NOF + 2ClF_3 \longrightarrow Cl_2 + 6NO_2F + 2NOF$
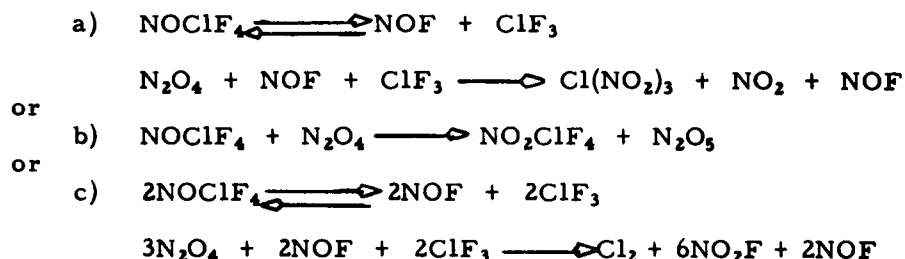
A reaction evidently occurred and the conditions and some results are shown in Table 9, Experiment 1089D-45. The products were distilled from the nickel reactor to a glass trap for further fractionation and, because of this, possible reaction of active fluorine compounds with glass cannot be excluded.

A small amount of white solid was observed in the Pyrex glass trap which contained 15.6% nitrogen and 47.5% fluorine. The small amount of solid available precluded complete identification. The results of this study were inconclusive.

(f) <u>NOClF₄ + AlF₃</u>

Material

NOClF₄. Prepared as above.

AlF₃. The Matheson Company, Inc.

Apparatus

The same as above.

Procedure

In a typical experiment, nitrosyl tetrafluorochlorate (0.216 mole) and aluminum fluoride (0.060 mole) were placed in the reactor and agitated for 16 hours at 25°C.

Results

It was anticipated that the preparation of a polyhalide salt of a multi-valent element such as aluminum might be achieved through a metathesis reaction involving aluminum fluoride and nitrosyl tetrafluorochlorate, i. e:

$$AlF_3 + 3NOClF_4 \longrightarrow Al(ClF_4)_3 + 3NOF \uparrow$$

The nitrosyl fluoride, being a gas at room temperature, could be easily removed leaving a pure aluminum tetrafluorochlorate salt.

The results and conditions of two experiments are shown in Table 9, Experiments 1089D-25, and 1089D-29. A reaction occurred and the amount of solid recovered at the end of the experiments was greater than the weight of starting aluminum fluoride. This would be expected if the desired reaction occurred; however, analyses did not support the presence of $Al(ClF_4)_3$ in the solid. Most notable was the complete absence of chlorine in the product. Analysis of the product from Experiment 1089D-25 showed,

		Found	Theoretical for $Al(ClF_4)_3$	Theoretical for $AlF_3 \cdot 2.74 NOF \cdot 1.72 F_2$
Wt.%	Al	9.37	7.4	9.51
	F	60.51	63.1	61.50
	Cl	0.0	29.4	0.00
	N	13.36	0.0	13.53
	O	15.30	0.0	15.46
		98.54	99.9	100.00

This result indicates that some unknown complex reaction may have occurred and the solid product may be a mixture of AlF_3, NOF and either fluorine or HF which could have formed by partial hydrolysis with traces of water. There is no reason, however, to suspect contamination with water.

The product from the second experiment, 1089D-29, was subjected to thermal decomposition in an effort to identify the various components present. The results of this fractionation are shown in Table 9A. This fractionation showed that chlorine is liberated from the product from -79°C. to 25°C. but the chlorine is not evolved as ClF_3. The product composition was not sufficiently elucidated by the fractionation technique employed and no firm conclusion can be made. However, the volatile nature of the chlorine suggests that either $Al(ClF_4)_3$ is not formed at all or the compound $Al(ClF_4)_3$ is formed but is unstable.

(g) <u>NOClF_4 + AlF_3 + N_2O_4</u>

Material

NOClF_4. Prepared as described.

AlF_3. Allied Chemical and Dye Corporation, General Chemicals Division.

N_2O_4. The Matheson Company, Inc.

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Apparatus

The same as above.

Procedure

Nitrosyl tetrafluorochlorate (0.168 mole), aluminum fluoride (0.06 mole) and dinitrogen tetroxide (0.284 mole) were placed in the reactor and agitated for 24 hours at 25°C.

Results

Various reaction schemes had been investigated in an attempt to prepare and isolate the compound $Al(ClF_4)_3$. All of the systems failed to produce the desired product. In this work N_2O_4 was expected to perform as a solvent for the metathesis reaction involving aluminum fluoride and nitrosyl tetrafluorochlorate:

$$3NO^+ClF_4^- + Al^{+++} + 3F^- \xrightarrow{N_2O_4} Al(ClF_4)_3 + NOF$$

The results of this work are shown in Table 9, Experiment 1089D-35. A reaction occurred but analysis of the solid again did not support the reaction shown above.

		Found	Theoretical for $Al(ClF_4)_3$	Theoretical for $AlF_3 2:04NOF \cdot 26F_2$
Wt. %	Al	13.1	7.4	13.9
	N	13.8	0.0	14.7
	F	51.0	63.1	54.5
	Cl	0.0	29.4	0.0
	O	15.8	0.0	16.9
		92.7	99.9	100.0

A possible decomposition leading to the complex solid mixture proposed is:

$$NOClF_4 + AlF_3 \xrightarrow{N_2O_4} AlF_3 + ClF\uparrow + F_2 + NOF$$

The fluorine might then complex with either the aluminum fluoride or the nitrosyl fluoride. This system did not produce any evidence for the desired product.
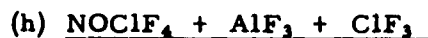
(h) NOClF_4 + AlF_3 + ClF_3

Material

NOClF_4. Prepared as described.

AlF_3. Allied Chemical and Dye Corporation, General Chemicals Division.

ClF_3. The Matheson Company, Inc.

Apparatus

The same as above.

Procedure

In a typical experiment nitrosyl tetrafluorochlorate (0.222 mole), aluminum fluoride (0.060 mole), and chlorine trifluoride (0.644 mole) were placed in the reactor and agitated for 16 hours at 25°C.

Results

Chlorine trifluoride was used as a solvent to promote solvation of nitrosyl tetrafluorochlorate and aluminum fluoride. It was expected that a metathesis reaction might occur as follows:

$$AlF_3 + NOClF_4 \xrightarrow{ClF_3} Al(ClF_4)_3 + 3NOF$$

$$3NOF + 3ClF_3 \longrightarrow NOClF_4$$
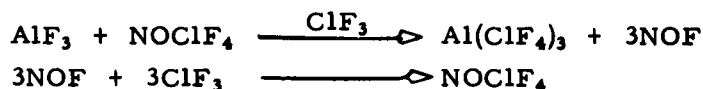
The results of five experiments listed in Table 9 show that a reaction occurred but the desired compound $Al(ClF_4)_3$ was not present in the solid product. Chlorine was evolved in these reactions either as Cl_2 or more probably as ClF. In every experiment analysis showed that the recovered solid was a complex mixture of AlF_3, NOF, and fluorine in varying amounts.

Addison (24) has reported the preparation of NO $AlClF_4$ but fluoro-aluminum complexes such as $NO^+AlF_4^-$ are not known. In reactions above, the nitrosyl tetrafluorochlorate might have decomposed initially to yield

$$NOClF_4 \longrightarrow NOF + ClF_3$$

The aluminum fluoride might then react with the nitrosyl fluoride,

$$NOF + AlF_3 \xrightarrow{ClF_3} NO AlF_4$$
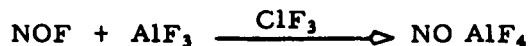
A second mole of NOF or possibly NOF complexed with HF might then react with the NO AlF_4. In these experiments there is no reason to suspect that HF might be present although contamination with water is always possible.

The nature of the solid products obtained in this work was not completely resolved but the absence of chlorine showed that the desired product $Al(ClF_4)_3$ was not present.

Section III. Reactions With $[ClF_2BF_4]$

1. Objectives

A reaction occurs between boron trifluoride and chlorine trifluoride to form a solid product containing one mole of boron trifluoride and one mole of chlorine trifluoride. Three possible structures were considered for this new compound i. e.

a. $ClF_3 \cdot BF_3$

b. $ClF_2^+ BF_4^-$

c. $BF_2^+ ClF_4^-$

Of the three structures (b) was thought to be the most probable since the infrared spectra showed absorption bands at 1030 and 1070 cm^{-1}, typical of the BF_4^- groups.

If the structure was indeed $ClF_2^+ BF_4^-$ it was reasoned that this new compound should undergo metathesis reactions. If this was so, then this compound might be more useful than other compounds containing the ClF_2 cation, such as $ClF_2^+ AsF_6^-$ and $ClF_2^+ SbF_6^-$, due to the stability of the BF_4 anion.

Several exploratory ion exchange reactions were conducted with this boron trifluoride-chlorine trifluoride adduct in an attempt to prepare several new oxidizers and to confirm the ionic structure of the adduct. The selected reactions are:

$$ClF_2^+BF_4^- \ + \ K^+NO_3^- \ \longrightarrow \ ClF_2^+NO_3^- \ + \ K^+BF_4^-$$

$$ClF_2^+BF^- \ + \ K^+ClO_4^- \ \longrightarrow \ ClF_2^+ClO_4^- \ + \ K^+BF_4^-$$

$$ClF_2^+BF_4^- \ + \ K^+ClO_4^- \ \longrightarrow \ ClF_2^+ClO_4^- \ + \ K^+KBF_4^-$$

$$2ClF_2^+BF_4^- + \ (K^+)_2NClO_3^= \ \longrightarrow \ (ClF_2^+)_2NClO_3^= \ + \ 2K^+BF_4^-$$

a. $[ClF_2BF_4]$ + KNO_3
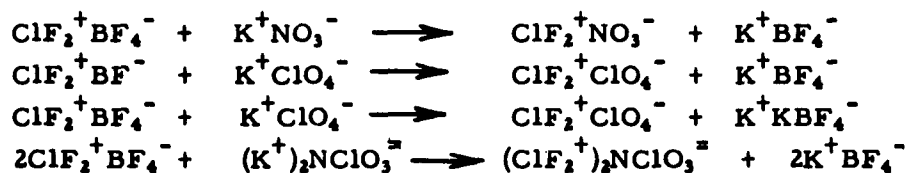
Material

$[ClF_2BF_4]$, prepared by the reaction of ClF_3 with BF_3, as described in Section 1A4b

KNO_3, Fisher Scientific Co.

Apparatus

The general purpose metal high vacuum line is described in Figure 1. The nickel reactor used is described in Figure 2.

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Procedure

[ClF$_2$BF$_4$] (0.025 mole) and KNO$_3$ (0.030 mole) were placed in the nickel reactor, Figure 2. The reactor was closed, placed on a mechanical agitator, and the reactants were agitated for 16 hours at 25°C. The product was then fractionated an analyzed.

A reaction occurred when the adduct [ClF$_2$BF$_4$] was added to KNO$_3$ and a white solid was recovered. Element analysis of the solid after removal of all volatile products in Experiment 1876D-84, Table 8, showed:

		Found	Theoretical for ClF$_2$NO$_3$	Theoretical for ClF$_2$NO$_3$+KBF$_4$	or	No Reaction
Wt. %	F	42.38	28.05	43.6		
	Cl	13.34	26.18	13.6		
	N	6.84	10.34	5.4		
	B	4.24	0.00	4.1		
	O	—	35.43	18.4		
	K	—		15.0		
				100.1		

If a reaction had occurred as shown in the above equation, there would have been no evolution of volatile product assuming that ClF$_2$NO$_3$ was also a solid. Only 78.8% of the starting reactants remained in the solid state in Experiment 1876D-84. The presence of KBF$_4$ was not confirmed.

A second experiment was conducted with identical conditions to provide more data on the reaction and product composition, Experiment 1089D-5, Table 8. In this case also a reaction evidently occurred to yield a solid and an unidentified gaseous product. Elemental analyses of the gaseous and solid products were obtained:

		Solid	Gas
Wt. %	N	5.1	5.1
	B	6.0	1.5
	F	50.8	21.6
	Cl	2.5	9.3

Mole ratios of elements in the solid product were:

O = 10.4

Cl = 1

N = 2.84

B = 5.38

K = 5.38

F = 25.84

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If one assumes that all of the potassium is present in the solid as KBF$_4$ then the remaining solid would consist of the following elements:

Cl = 1

N = 2.84

F = 4.32

O = 10.4

Comparison of the data from two experiments showed that the solid was not reproduced under identical conditions. It was not established whether ClF$_2$NO$_3$ was formed and perhaps decomposed in one case but not in another.

The structure of the adduct [ClF$_2$BF$_4$] was not defined as a result of this preliminary effort.

b. [ClF$_2$BF$_4$] + KClO$_4$

Material

[ClF$_2$BF$_4$], prepared as described in Section (1A4b).

KClO$_4$, Fisher Scientific Co.

HF, Merck and Company, Reagent Grade.

Apparatus

The general purpose metal high vacuum line is described in Figure 1. The nickel reactor is described in Figure 2.

Procedure

In a typical experiment 0.018 mole of [ClF$_2$BF$_4$] and 0.22- mole of KClO$_4$ were placed in the nickel reactor, Figure 2. The reactor was then evacuated, closed, and placed on a mechanical agitator (Burrell Shaker). The reactants were agitated for 16 hours at 25°C. or 48 hours at 50°C. The product was then fractionated and analyzed.

Results

The results of two experiments 18760-65, and 1876D-68 are listed in Table 8.

The objective of this work was two-fold: (a) to provide additional data on the structure of the boron trifluoride-chlorine trifluoride adduct and (b) to prepare a new oxidizer ClF$_2$ClO$_4$ by the following reaction:

$$ClF_2^+BF_4^- + K^+ClO_4^- \longrightarrow KBF_4 + ClF_2^+ClO_4^-$$
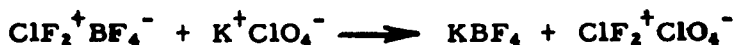
In experiment 1876D-65 a reaction occurred at 25°C. to yield a solid product and a gaseous product. The gaseous product consisted mainly of

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ClO_3F with smaller concentrations of an unidentified substance that showed infrared absorption bands at 9.7 and 10.55μ. Partial chemical analysis of the solid showed no chlorine and a boron content of 6.89%. The complete absence of chlorine in the solid, coupled with the liberation of ClO_3F, indicated that the desired product ClF_2ClO_4 either did not form or decomposed.

In experiment 1876D-68 the reactants were agitated for 48 hours at 50°C. in the presence of hydrogen fluoride as solvent. In this experiment it was hoped that the solvent would promote the desired reaction and prevent decomposition of the ClF_2ClO_4.

$$ClF_2{}^+BF_4{}^- + K^+ClO_4{}^- \xrightarrow{HF} ClF_2ClO_4 + KBF_4.$$

A reaction occurred under these conditions but again there was no evidence that ClF_2ClO_4 was produced. The presence of the solvent complicated the analysis, especially of the volatile products which remained in the HF fraction. On the basis of boron content of the solid, 61 weight per cent of the boron remained in the solid phase probably as KBF_4 or $KBF_4 \cdot XHF$.

c. $[ClF_2BF_4] + K_2NClO_3$

Material

$[ClF_2BF_4]$, prepared as described in Section (1A4b).

K_2NClO_3. This compound was prepared by the following reactions(90):

$$3NH_3 + ClO_3F \xrightarrow{NH_3} NH_4NHClO_3 + NH_4F$$

$$NH_4NHClO_3 + KOH \xrightarrow{NH_4OH} K_2NClO_3 \downarrow + NH_3 \uparrow + H_2O$$
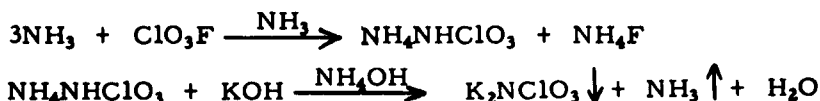
The precipitate was then washed with methanol to remove NH_4OH and H_2O and then dried in a vacuum oven at room temperature. The dried salt was very shock sensitive and elemental analysis indicated that a small amount of impurity, possibly KOH, was present.

		Found	Theoretical
Wt%	K	48.75	44.5
	N	8.3	8.0
	Cl	18.9	20.2
	O		27.3
			100.0

Apparatus

The general purpose metal high vacuum line is shown in Figure 1. A typical nickel reactor used in this experiment is shown in Figure 2.

Procedure

Potassium imidochlorate (0.011 mole) and $[ClF_2BF_4]$(0.014 mole)

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were placed in the nickel reactor, Figure 2. The reactor was evacuated, closed, and placed on a mechanical agitator (Burrell Shaker) and the reactants were agitated for 16 hours at 25°C. The product was then fractionated and analyzed.

Results

This work was directed toward effecting replacement of the potassium ions with two ClF_2 cations by the following reaction:

$$K_2^+NClO_3^= + 2ClF_2^+BF_4^- \longrightarrow (ClF_2^+)_2NClO_3^= + KBF_4$$

It was expected that the formation of KBF_4, a very stable configuration, would promote this reaction.

The results of this work are shown in Table 8, Experiment 1876D-77. A reaction occurred to yield solid and volatile products. The volatile products were identified by infrared analysis as NO_2F and possibly OF_2. Some unidentified gas exhibiting infrared absorption bonds at 8.25 and 9.05μ was also detected.

The solid product could not be identified on the basis of elemental analysis since it probably consisted of more than one compound. The expected reactivity of this solid also rendered fractionation by conventional solvent extraction techniques more difficult. A boron analysis of the solid showed that 73.4 weight per cent of the starting boron remained in the solid and the B:F ratio in the recovered solid was 1:27 respectively. This indicated that the desired compound $(ClF_2)_2NClO_3$ was not present. The volatile product NO_2F could have resulted from decomposition $(ClF_2)_2NClO_3$.

Section IV. Reactions with Chlorine Oxides

A. Reactions with Cl_2O_7

1. Objective

Reaction of chlorine heptoxide with tetrafluorohydrazine, difluoramine and chlorodifluoramine was considered to be a potential route to the unknown oxidizers NF_2ClO_4 and NF_2ClO_3. In particular, approaches utilizing inert solvents such as carbon tetrachloride appeared feasible because most of these reagents are soluble in solvents of such nature and chlorine heptoxide can be handled safely when dissolved in carbon tetrachloride. In addition, if covalent bonding is involved, the compounds NF_2ClO_4 and NF_2ClO_3 should be soluble in such inert solvents.

Earlier studies, both at Olin and elsewhere, had suggested that chlorine heptoxide and tetrafluorohydrazine interact. In the presence of Pyrex glass side reactions occur obscuring the reaction of interest. Consequently, the reactions were investigated in metal or Teflon systems.

a. Cl_2O_7 + N_2F_4

Material

Cl_2O_7 (not distilled). Chlorine heptoxide was prepared by the method of Meyer and Kessler (33). In a typical preparation, 400 ml. of reagent grade carbon tetrachloride is placed in a Waring Blender and stirred vigorously. Phosphorous pentoxide (40 g.) is then added to the blender followed by 15 ml. of 70% perchloric acid. The blender contents are cooled to 0°C. and stirred for an additional 30 minutes. The slurry is then filtered through a fritted glass filter. A sample of the filtrate is hydrolyzed and titrated with standard base to determine the concentration of chlorine heptoxide. Generally, the solution contains 1% by weight of chlorine heptoxide. Infrared analysis of the solution could not detect any impurities.

Cl_2O_7 (distilled). In a typical preparation, 120 ml. of reagent grade carbon tetrachloride and 50 g. of phosphorus pentoxide are placed in a round bottom Pyrex flask equipped with a mechanical stirrer (Figure 13). The mixture is cooled to 0°C. and 8.2 g. of 70% perchloric acid is added dropwise with stirring while the temperature is maintained 0°C. The reactants are stirred for an additional 30 minutes and then 30 ml. of carbon tetrachloride removed by distillation under reduced pressure. The remaining reactor slurry is gradually heated to 65-70°C., held at this temperature for 30 minutes and stirred constantly. The temperature is then increased to 76°C. and the carbon tetrachloride-chlorine heptoxide distillate collected in a receiver maintained at -20°C. The distillation is stopped after approximately 75 ml. of distillate is collected. In some preparations the distillate is pale yellow in color. This coloration is due to dissolved chlorine oxides which are removed by heating the distillate for several minutes to its boiling point under

Figure 13

Apparatus for Preparation of Distilled Chlorine Heptoxide
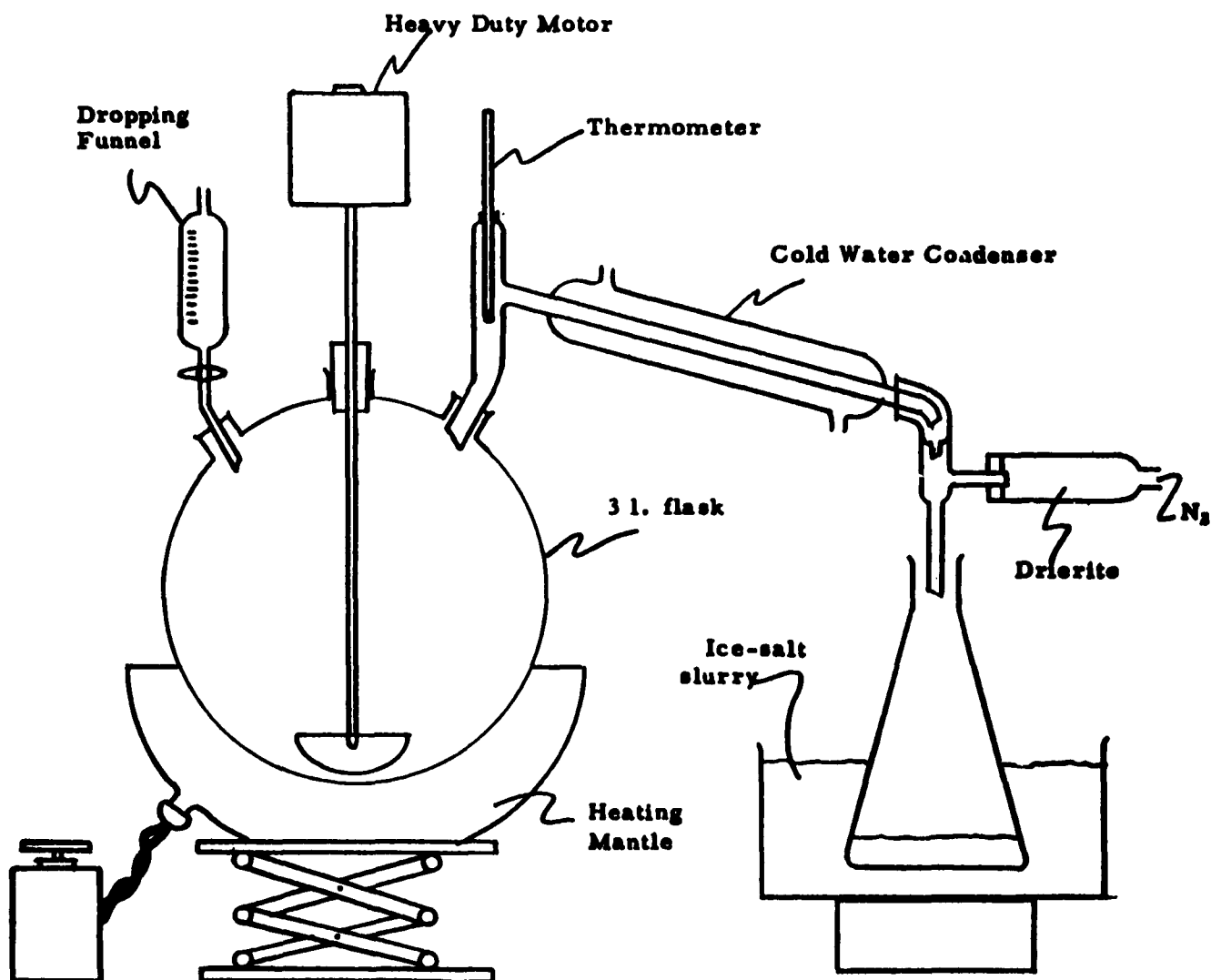
atmospheric pressure. The final product is a colorless solution consisting of 7-8 per cent by weight of chlorine heptoxide.

N_2F_4. The tetrafluorohydrazine was used as received from Stauffer Chemical Corporation, Chauncey, New York, and E. I. DuPont de Nemours and Co., Inc., Gibbstown, New Jersey. Typical analyses from the respective suppliers are listed below:

	Stauffer Wt. %	DuPont Wt. %
N_2F_4	87.70	99.20
C_2F_6	11.33	0.00
NF_3	0.26	0.20
NO_2	0.46	0.00
N_2	0.27	0.06
N_2O	0.00	0.30
NO	0.00	0.24
	100.02	100.00

Apparatus

Two reactor designs were used in this work. The Teflon reactor (Figure 15) consisted of a 600 ml. Teflon machined vessel with a solid Teflon cap. The cap was held in place by a metal collar. A 1/4 inch diameter polyethylene tube was connected to the Teflon cap through a Swagelocke nylon tube fitting. To eliminate metal entirely, the reactor was closed by collapsing the polyethylene tubing with a clamp.

The metal reactor consisted of a Hoke one-liter 304 stainless steel spun cylinder equipped with a 304 stainless steel Teflon gasketed needle valve.

These reactors were attached to the material transfer high vacuum line (Figure 14) for loading or removal of volatile products.

Procedure

In a typical experiment, the reactor was cleaned and dried and then placed in a nitrogen dry box. Chlorine heptoxide, dissolved in carbon tetrachloride, was placed in the reactor. In some experiments a catalyst, such as water or metal filings, was added to the solution. The reactor was then closed and connected to the material transfer line. A steel cylinder, containing a weighed amount of tetrafluorohydrazine was also attached to the line.

The reactor was cooled to -78°C. and the nitrogen pumped out. The -78°C. bath was then removed and the reactor cooled to -196°C.

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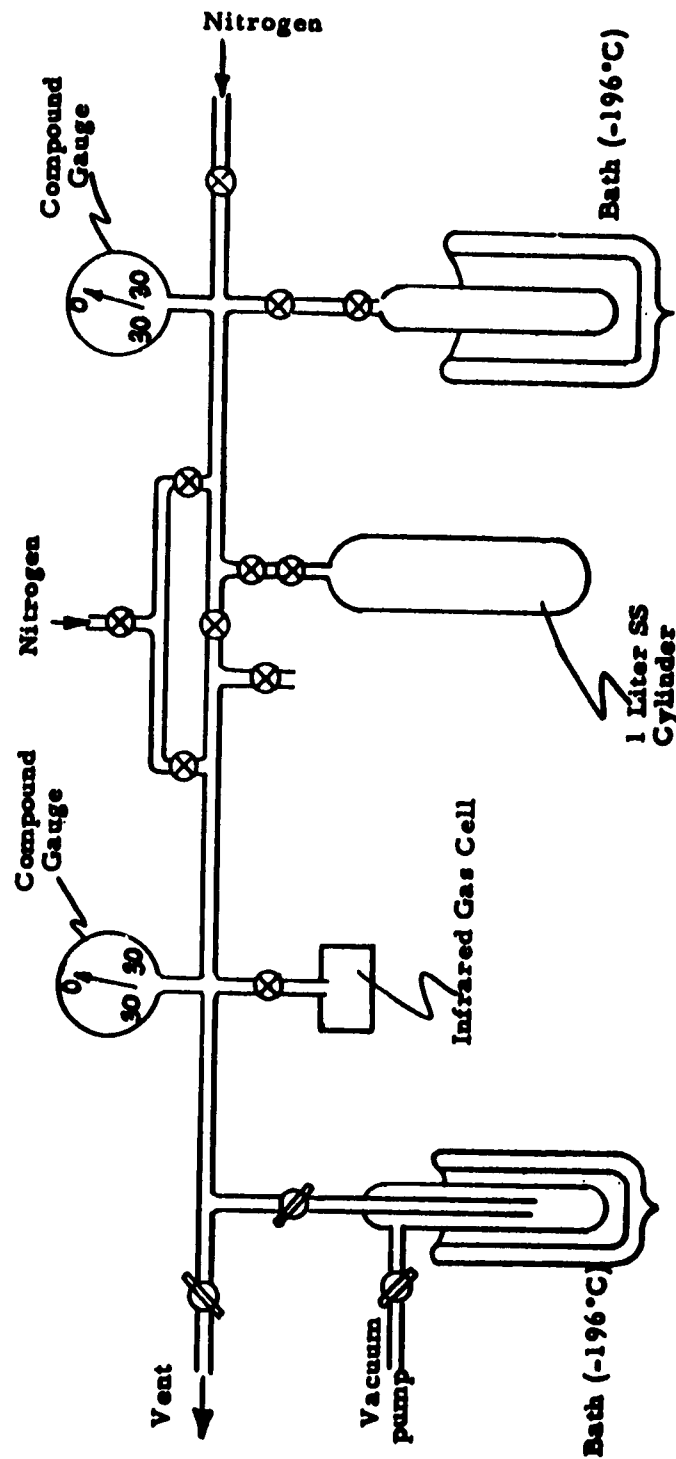
Figure 14

High Vacuum Material Transfer Line

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Figure 15

Teflon Reactor

- Brass Flare fitting nut
- Pinch clamp
- "Polyflo" Tubing
- Nylon Nut
- Teflon plug
- Metal Collar
- 600-ml. Teflon Cylinder
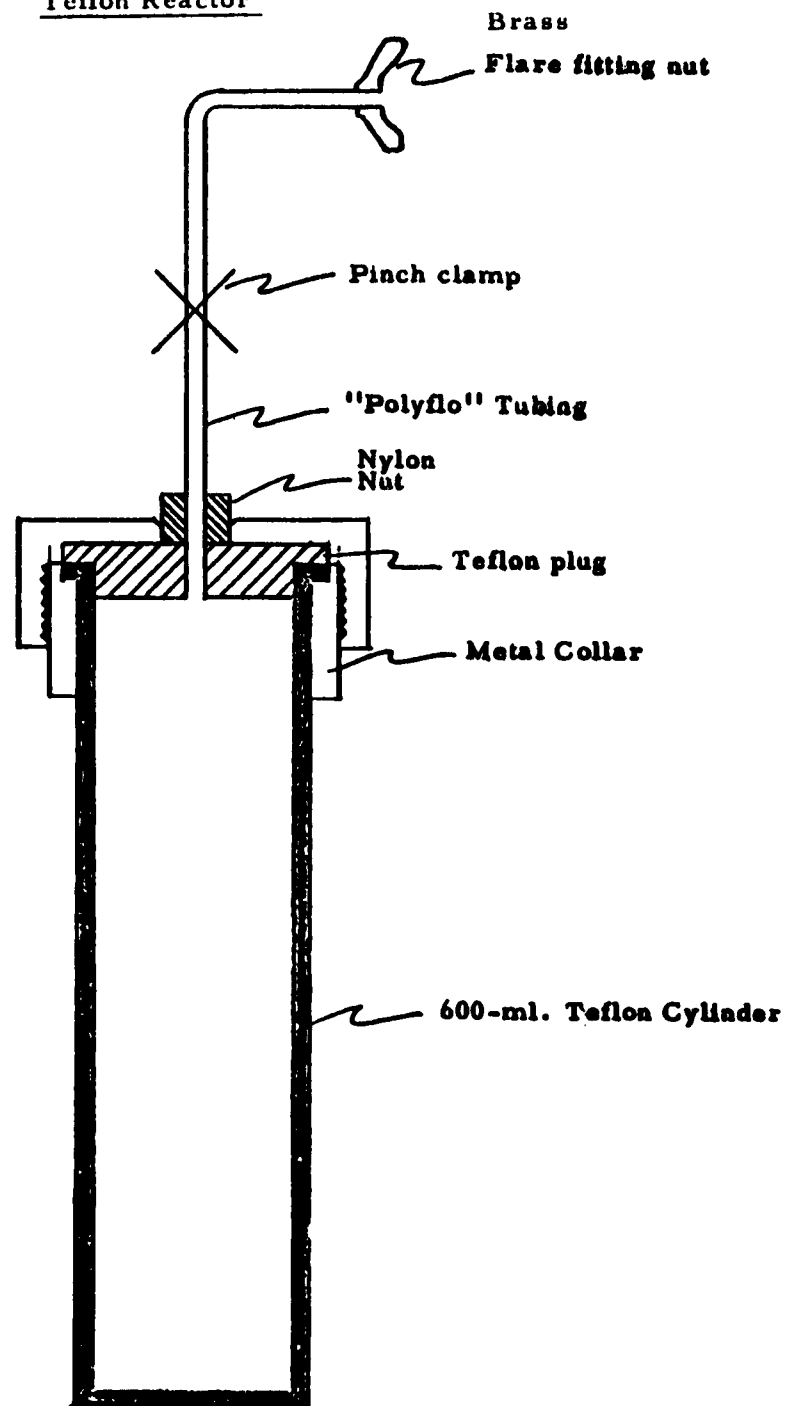
The tetrafluorohydrazine was then added to the reactor. The reactor was permitted to stand at the desired temperature for the specified time. In some experiments the reactor was rocked to provide agitation. The products were then fractionated and analyzed.

Results

Over two hundred experiments were conducted on the reaction of chlorine heptoxide with tetrafluorohydrazine. Since a considerable number of these were designed solely for the purpose of providing product for characterization and, therefore,were exact duplicates, only the more pertinent experiments are listed in Tables 25, 26, 27, 28, 29, 30, 31.

The objective of this investigation was to study the reaction

$$Cl_2O_7 + N_2F_4 \xrightarrow{\quad CCl_4 \quad} NF_2ClO_4 + NF_2ClO_3$$

A crystalline white solid generally precipitated from the carbon tetrachloride solution but in low yields (approximately 10%). The product from ten of these experiments (Table 25) was combined and the composite solid sample 1462-9, Table 32, subjected to extensive analysis.

		Found	Theoretical for NF_2ClO_4	Theoretical for $(NF_2ClO_4 + NF_2ClO_3)$
Wt. %	F	22.2	25.1	26.5
	Cl	22.4	23.4	24.7
	N	8.5	9.2	9.8
	O		42.3	39.0
			100.0	100.0

The initial analytical results were encouraging, particularly since there had been no previous purification of the product.

A portion of this same product was ashed in a platinum boat to determine whether the fluorine might be bonded to metals, perhaps from the stainless steel reactor. A 2.7 per cent by weight ash was obtained, which consisted of metal oxides. The actual metal content was then considerably less than 2.7 per cent since the combined oxygen was expected to contribute possibly one-half to the total ash depending on the particular metal oxides present. Emission spectrographic analysis of the ash detected iron, nickel, chromium and phosphorus as major constituents. The metals were undoubtedly due to some interaction with the stainless steel reactor and the phosphorous was thought to be carried over from the carbon tetrachloride solution. While these concentrations of iron, chromium and nickel were too low to account for the 22 wt. per cent fluorine in the solid, it was feared that higher concentrations of phosphorous might be present but was being lost during ashing.

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Table 25

Reaction of Chlorine Heptoxide and
Tetrafluorohydrazine

	Reactants Used (g.)		Reaction Conditions			Solid	Solid
Experiment No.	Cl_2O_7	N_2F_4	Temp. °C	Reaction Time (hrs.)	CCl_4 (ml.)	Solid Product (g.)	Solid Product ** Yield (%)
1462 - 1a	3.07	6.0	25	22	450		
- 1b	5.65	6.0	25	22	475		
- 4a	3.65	5.0	25	18	415		
- 4b	3.14	6.3	25	18	500		
- 4c	3.44	6.3	25	18	425	12.5	11.2
- 4d	4.17	6.3	25	18	510		
- 6a	4.07	6.0	25	18	510		
- 6b	4.81	5.0	25	18	600		
- 6c	5.78	5.0	25	18	580		
- 6d	2.77	6.0	25	18	550		
- 6e	6.41	8.0	25	18	510		
- 22a	6.41 *	10.0	25	18	400	4.4	
- 24a	6.41	7.0	25	18	400	0.3	
- 24b	6.41	7.0	25	18	400	0.5	
- 24c	6.41	7.0	25	18	400	0.7	
- 24d	6.41	7.0	25	18	400	0.5	
- 26a	6.31	7.0	25	18	400	trace	
- 26b	6.77	7.0	25	18	400	0.3	2.2
- 27a	3.50	8.0	25	18	400	1.4	12.2
- 27b	6.34	8.0	25	18	400	0.3	2.1
- 27c	7.03	8.0	25	18	400	0.3	2.0
- 33a	3.80	6.0	25	24	400	0.9	9.2
- 33b	3.39	8.5	25	24	400	2.9	24.4
- 33c	4.20	6.5	25	24	400	2.0	18.7
- 33d	3.72	7.0	25	24	400	3.8	35.4
- 37a	3.59	7.5	25	18	400	3.9	35.2

* Amount of Cl_2O_7 in expts. - -22a through -24d estimated to be the same as in -6e.

** Yield = $\dfrac{\text{g. Product}}{\text{g. Reactant } (Cl_2O_7 + N_2F_4)}$

Table 26

Reaction of N_2F_4 + Undistilled Cl_2O_7

Experiment No.	Reactants (g.)		Experiment Conditions				Solid Product g.	Analysis of Solid Product				
	N_2F_4	Cl_2O_7	T°C	Reaction Time (Hrs.)	Solvent CCl_4(g.)	Reactor Type		F	F (Hydrolyzable)	Cl	N	P
1462-21	8.0	---(b)	25	18	400	Poly-propylene	2.0	14.9	---	19.6	8.6	---
1462-22d	10.0	---(b)	25	18	500	S. Steel	2.2	25.6	---	18.9	8.1	---
1462-32a	8.0	---(b)	25	20	500	S. Steel	0.7					
1462-32b	8.5	---(b)	25	20	480	S. Steel	0.8	3.0	---	12.7	10.7	---
1462-32c	8.0	---(b)	25	20	450	S. Steel	0.4	(a)				
1462-32d	9.5	---(b)	25	20	455	S. Steel	0.6					
1462-39a	7.0	2.9	25	20	437	S. Steel	1.2	15.6	7.7	---	---	---
1462-39c	4.0	6.5	25	20	540	S. Steel	0.9	1.6	0.4	---	---	---
1462-41a	8.0	4.1	25	20	495	S. Steel	2.5	13.9	11.4	---	---	---
1462-41b	7.0	5.1	25	20	500	S. Steel	3.9	28.0	9.9	---	---	---
1462-41c	8.0	2.7	25	20	435	S. Steel	3.7	33.9	11.4	---	---	---
1462-41d	9.0	3.9	25	20	455	S. Steel	3.4	30.6	12.6	---	---	---
1462-41g	5.5	4.4	25	18	470	S. Steel	2.7	19.7	2.3	---	---	---
1462-43a	3.0	4.8	25	18	490	S. Steel	1.5	3.4	0.4	---	---	0.8
1462-43b	6.0	5.2	25	18	425	S. Steel	0.7	5.7	2.1	---	---	0.6
1462-43d	6.0	7.4	45	18	365	S. Steel	0.7	7.9	0.8	---	---	1.9
1528-52a	6.5	3.7	25	18	440	S. Steel	0.9	15.1	14.3	---	---	0.0
1528-52b	5.0	4.9	25	18	450	S. Steel	2.1	10.5	7.4	---	---	0.5
1528-52d	7.0	10.7	25	18	460	S. Steel	4.3	12.1	11.0	---	---	0.0
1528-52e	3.0	4.2	25	18	460	S. Steel	1.6	13.5	13.4	---	---	0.9
1528-52g	5.5	8.8	25	18	385	S. Steel	2.7	3.7	2.2	---	---	0.1
1528-52h	3.0	9.8	25	18	460	Poly-propylene	1.0	4.1	0.4	---	---	0.0
1528-61a	6.0	3.5	25	20	525	S. Steel	1.5	15.1	5.2	---	---	1.1
1528-61b	5.0	3.5	25	20	545	S. Steel	1.4	30.7	13.6	---	---	5.9

(a) Products were combined before analysis.
(b) Not determined.
  N_2F_4 used as received from Stauffer Chemical Corporation.
** CCl_4 used as received from supplier.

Table 27

Reaction of N_2F_4 + Distilled Cl_2O_7

| Experiment No. | Reactants (b)(g.) | | Reaction Conditions | | | | | Solid Product g. | Analysis of Solid Product Wt % F |
	N_2F_4	Cl_2O_7	T°C	Reaction Time (Hrs.)	Solvent CCl_4 (g.)(a)	Reactor Type	Agitation		
1528-55a	7.0	0.8	25	18	400	S. Steel	None	0	---
1528-55b	9.5	0.8	25	18	400	S. Steel	None	0	---
1528-62b	6.0	3.6	25	18	350	S. Steel	None	Trace	---
1528-62c	7.0	5.4	25	18	400	S. Steel	None	0.4	0.2
1528-64c	5.5	1.6	25	20	400	S. Steel	None	0.6	5.2
1528-57c	4.0	1.6	25	14	300	S. Steel	None	Trace	---

(a) CCl_4 used as received from supplier.
(b) Used as received from Stauffer Chemical Corporation.

Table 28

Additional Reactions of N_2F_4 with Cl_2O_7

Experiment No.	Reactor Charge (g.)				Reaction Conditions			Solid Product (g.)	Analysis of Product				
	N_2F_4	Cl_2O_7	CCl_4	Other	T°C	Time Hrs.	Reactor Type		F Total	F (Hydrolyzable)	Cl	N	P
1528-55c	8.0S	0.9*	640*	--	25	18	S. Steel	0	--	--	--	--	--
1528-55d	5.5S	0	640*	--	25	18	S. Steel	0	--	--	--	--	--
1528-57a	4.5S	3.1*	752*	--	25	14	S. Steel	3.1	28.0	11.8	--	--	--
1528-57b	5.0S	5.5*	752*	--	25	14	S. Steel	0.1	4.1	1.8	--	--	--
1528-57c	5.0S	0	640*	--	25	14	S. Steel	0	--	--	--	--	--
1528-57d	5.5S	0	640*	(a)	25	14	S. Steel	3.4	3.7	--	--	--	39.4
1528-57f	2.5S	1.6*	440*	--	25	14	S. Steel	0	--	--	--	--	--
1528-62a	8.0S	3.6*	640*	--	25	18	S. Steel	0.1	3.5	--	--	--	--
1528-66	16.5S	3.7*	496*	--	9-20	56	S. Steel	0.2	4.6	--	47.4	10.8	--
1528-78	6.0D	4.3**	707**	(b)	25	16	Teflon	0.9	14.0	13.3	--	--	--
1516-25	6.7D	4.3**	707**	(c)	25	16	Teflon	0.53	27.6	26.8	--	--	--
1516-17	6.7S	4.3**	707**	(d)	25	32	Teflon	1.0	13.7	--	19.3	7.4	2.9
1738D-32	6.6S	4.3**	707**	(e)	25	40	Teflon	1.0	13.8	--	15.3	5.9	3.2
1738D-34	6.5S	4.3**	707**	(f)	25	20	Teflon	1.5	15.5	--	18.6	7.5	2.4

* Not distilled
** Distilled
D Used as received from DuPont
S Used as received from Stauffer

(a) 4.0 g. P_2O_5
(b) 0.15 g. H_2O, 5.1 g. Ca turnings
(c) 0.33 g. FeF_3, $3H_2O$
(d) 0.1 g. P_2O_5, 0.15 g. H_2O
(e) 0.1 g. P_2O_5, 0.15 g. H_2O, 0.21 g. 304 S. Steel filings
(f) 0.1 g. P_2O_5, 0.15 g. H_2O, 0.20 g. 304 S. Steel filings

Table 29

Effect of Water and Metals
(agitation)

Experiment No.	Reactants (g.)				Reaction Conditions			Solid Product (g.)	Analysis of Product	
	N_2F_4	Cl_2O_7	H_2O	No. 304 S. Steel Filings	T°C	Reaction Time (Hrs.)	Solvent CCl_4(g.)		F	F (Hydrolyzable)
1516-26a	6.3D	4.3	0.15	0.21	25	17	707	0.473	11.5	11.5
1516-26b	6.9D	4.3	0.15	0.21	25	17	707	0.497	16.7	16.9
1516-26c	6.6D	4.3	0.15	0.21	25	17	707	0.595	7.4	7.3
1516-26d	6.7D	4.3	0.15	0.21	25	18	707	0.410	5.1	5.4
1859D-89	6.4D	4.3	0.15	0.20	25	16	707	0.49	5.4	5.3
1516-28a	6.4D	4.3	0.15	0.21	25	16	707	1.014	9.4	9.6
1516-28b	6.4D	4.3	0.15	0.21	25	16	707	1.104	7.6	7.8
1516-28c	6.4D	4.3	0.15	0.21	25	17	707	0.606	11.5	10.9

D = DuPont N_2F_4

Table 30

Effect of Water and Metals
(no agitation)

Experiment No.	Reactants (g.)				Reaction Conditions			Solid Product (g.)	Analysis of Product	
	N_2F_4	Cl_2O_7	H_2O	No. 304 S. Steel Filings	T°C	Reaction Time (Hrs.)	Solvent CCl_4(g.)		F	F (Hydrolyzable)
1859D-86	6.7S	4.3	0.15	0.20	25	16	707	1.26	9.4	9.0
1516-21	6.7S	4.4	0.15	0.20	25	16	707	1.47	7.7	---
1537-13	6.5S	4.4	0.15	0.20	25	16	707	1.31	13.1	7.4
1738D-39	6.6D	4.3	0.25	0.20	25	17	707	0.679	1.5	1.4
1528-77	6.6S	4.3	0.25	0.21	25	17	707	1.143	17.9	17.5
1516-23	6.6S	4.3	0.25	0.20	25	16	707	0.555	4.1	4.1
1859D-88	6.4D	4.3	0.25	0.21	25	16	707	0.821	13.2	13.1
1738D-40	6.6D	4.3	0.15	0.20	25	16	707	1.150	10.7	10.5
1738D-41	6.6D	4.3	0.15	0.20	25	16	707	0.992	5.8	5.3
1528-79	6.1D	4.3	0.15	0.20	25	16	707	0.77	11.4	11.5

D = DuPont N_2F_4
S = Stauffer N_2F_4

Table 31

Additional Experiments with Water and Metal

Experiment No.	Reactants (g.)				Reaction Conditions			Solid Product (g.)	Analysis of Product	
	N_2F_4	Cl_2O_7	H_2O	No. 304 S. Steel Filings	T°C	Reaction Time (Hrs.)	Solvent CCl_4 (g.)		F	F (Hydrolyzable)
1601-1	25.0D	20.0	0.7	(b)	25	20	3320	1.7	13.0	12.8
1516-30a	6.1D	4.3	0.15	0.20	25	17	707	1.0	5.0	5.3
1516-30b	6.1D	4.3	0.15	0.19	25	17	707	1.2	12.1	12.4
1516-30c	6.2D	4.3	0.15	0.21	25	17	707	0.8	12.1	11.8
1516-33a	6.6D	4.3	0.15	0.20	25	17	707	0.9		
1516-33b	6.0D	4.3	0.15	0.19	25	17	707	0.4 (a)	12.7	---
1516-33c	6.4D	4.3	0.15	0.22	25	17	707	0.7		
1516-35a	6.4D	4.3	0.15	0.24	25	17	707	0.6		
1516-35b	6.2D	4.3	0.15	0.20	25	17	707	0.8 (a)	10.4	10.7
1516-35c	6.1D	4.3	0.15	0.21	25	17	707	0.9		
1859D-83 (c)	6.7S	4.3	0.15	0.21	25	17	707	1.5	9.4	---
1528-75 (c)	6.7S	4.4	0.15	-	25	16	707	0.7	1.6	---
1859D-87 (c)	6.9S	4.3	0.25	0.20	25	4 1/3	707	0.8	3.5	3.2

(a) Products combined before analysis
(b) Reactor made of 316 stainless steel
(c) These mixtures not agitated

D = DuPont N_2F_4
S = Stauffer N_2F_4

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NH-2090

Table 32

Analyses of Oxidizer Products

Sample No.	Product Source	% Fluorine Total	Ionic	% Chlorine Total	Ionic	%Nitrogen	%Ash	Remarks
1462-9	1462 - 1a, -1b, -4a, -4b, -4c, -4d, -6a, -6b, -6c, -6d, -6c	22.17	0	22.42	0	8.5	2.7	
1462-22a	1462 - 22a	14.15		24.55		7.17		4.27% P
1462-22d	1462 - 22d	25.57		18.9		8.07		
1462-24	1462 - 24a, - 24b - 24c, - 24d	2.39		28.41		9.33		
1462-27A	1462 - 27a	14.83		17.95				
1462-27b	1462 - 27b	2.9		27.01				
1462-27c	1462 - 27c	0.3		27.26				
1462-34	1462 - 33a, - 33b, - 33c, - 33d	26.9		10.57		8.68		6.05% P
1462-38	1462 - 37a	31.43, 31.15	3.79					Sample consisted of white particles iso-lated from mixture of light green and white product.

A portion of the solid product was treated with aqueous sulfuric acid in a closed vessel to convert any volatile form of phosphorous or other impurity present to the more stable phosphates or sulfates. This solution was then ashed in a platinum boat at 600°C. The ash content was essentially the same (2.7 wt. per cent) and consisted of iron, chromium, nickel and phosphorus, in the form of oxides.

Infrared analysis of the solid as a mull showed absorption bands in the perchlorate and N-F region but the bands were too broad for reliable interpretation. The presence of a perchlorate group was reasonably established but the presence of N-F bonds was questionable. X-ray powder patterns were obtained but no identification was possible. The solid was noted to react with the glass capillary sample tubes.

A portion of the solid was then dissolved in water and the resulting solution analyzed by nuclear magnetic resonance in an attempt to detect the presence of N-F bonds (if complete hydrolysis did not occur) or the nature of the fluorine bonding after hydrolysis. Fluorine resonance signals were not detected even though the presence of fluorine was established by elemental analysis. Failure of the NMR to detect fluorine was attributed to either the low concentration of fluorine present in the aqueous solution or to the presence of iron which would tend to flatten out the fluorine signal.

A portion of the solid was next dissolved in water and titrated with standard base. If the oxidizer were NF_2ClO_4, it was expected to hydrolyze to two acids, similar to the hydrolysis of nitronium perchlorate:

$$NO_2ClO_4 + H_2O \longrightarrow HONO_2 + HClO_4$$

$$NF_2ClO_4 + H_2O \longrightarrow HONF_2 + HClO_4$$

A neutral equivalent of 76.85 was found. Assuming the hydrolysis above, this corresponds to a molecular weight of 153.7 (Theoretical for NF_2ClO_4:151.5).

On the basis of this combined data and with the observed reactivity of the product (hypergolic with 64% aqueous hydrazine) it was concluded that the product contained nitrogen, covalent fluorine, and chlorine in approximately the same proportion as that required for NF_2ClO_4. While the structure of this product was not confirmed, the presence of a perchlorate was indicated by infrared. The empirical formula $[NF_2ClO_4]$ was tentatively assigned to this formula.

It soon became evident that the product from the reaction of chlorine heptoxide with tetrafluorohydrazine was not reproducible. Wide variability, both in yield and fluorine content, indicated that the controlling parameters of this reaction were not known. Possible factors thought to be involved in the reaction were:

a. traces of water,

b. catalysis by impurities present in reactants,

c. catalysis by reaction material (stainless steel),

d. incompatibility of the desired product with other products,

e. instability of the desired product itself.

If the reaction actually involved some unknown catalytic activity, it was believed that the critical catalyst and/or conditions could be most expediently found by conducting a statistical study of the more probable variables. The effect of the variables, water, stainless steel and phosphorous pentoxide then was determined.

Two levels for each variable were chosen, thus making the study of the three variables an n-factorial design requiring 2^3 or 8 experiments. The low level for each variable was zero and the high levels for water, phosphorous pentoxide, and 304 stainless steel were 0.15 g., 0.10 g., and 0.20 g., respectively. The water and metal levels were more or less arbitrary ones with the P_2O_5 level being such that there would still be P_2O_5 remaining in the reactions where water was introduced. Since the reactions now were being conducted in the Teflon reactors, the stainless steel was added in the form of metal filings taken directly from a cylinder. The temperature chosen was 25°C. and the reaction time was 16 hours. Temperature was not treated as a variable because the temperature had not varied appreciably in the previous experiments which produced variable products and also because the effect of the reaction rate would be compensated by the long reaction time. The concentrations chosen for tetrafluorohydrazine and chlorine heptoxide were the same as those used in the early experiments. The quantities of reactants and solvent then were fixed at 4.26 g. of chlorine heptoxide, 6.54 g. of tetrafluorohydrazine and 707 g. of carbon tetrachloride. The reagents used were the purest obtainable. A vapor phase chromatogram of the Cl_2O_7 showed it to be free of perchloric acid and any other oxides of chlorine. The carbon tetrachloride was dried and distilled immediately before use.

The procedure used was the same as that already described. Products obtained from experiments which included metal filings were first dried and weighed with all the solids that had been removed from the reactor. These were then separated from as much steel filings as possible by shaking the solids in a Teflon beaker with the reaction liquid. Table 33 lists the results of this study. None of the products obtained had elemental analyses corresponding to the theoretical values for NF_2ClO_4. Furthermore, the material obtained from each experiment was a mixture of compounds. Therefore, no really adequate criteria for improvement in the reaction conditions to produce NF_2ClO_4 was available. As a substitute, the fluorine content was used as the response variable in an analysis of variance to determine the effect of the three variables and of their interactions. The usual calculations were performed and the results are found in Table 34. Only one variable, representing presence of the metal filings, has a variance greater than the residual and, therefore, any significant effect on the total fluorine. The residual variance was recalculated (20.8025) and the

Table 33

Statistical Evaluation of Variables

Exp. No.	VARIABLES			Product (g.)	Product Analysis (%)					Metal Recovered
	H_2O	P_2O_5	304 SS		F	Cl	N	P	C	
1528-68	+	+	-	0.699	11.9	10.20	8.99	4.23	0	
1738D-26	-	+	-	0.265	2.47	8.30	4.39	13.14	0	
1859D-78	+	-	-	0.150	3.82	13.73	8.41	0	0	
1859D-80	-	-	-	0.039	7.68					
1859D-82	+	-	+	0.970	15.0	10.19	12.14	0	0	68.9
1738D-28	-	+	+	0.765	12.9	14.63	5.36	3.56	0	94.6
1738D-30	+	+	+	1.050	17.1	14.99	5.69	3.37	0	97.5
1528-71	-	-	+	0.299	5.87	5.61	0.95	0	0	114.2

Reactants

4.26 g. Cl_2O_7
6.54 g. N_2F_4
707 g. CCl_4

Variables

$H_2O+ = 0.15g.$
$H_2O- = None$

$P_2O_5+ = 0.10g.$
$P_2O_5- = None$

$304ss+ = 0.20g.$
$304ss- = None$

Conditions

T°C. ± 25°C.
Reaction Times 16 hrs.
Teflon Reactor

Table 34

Analysis of Variance

Source of Variance	Degrees of Freedom	Sums of Squares	Mean Squares	Components of Variance
Between B (P_2O_5)	b-1 = 1	18.000	18.000	$ac\sigma_b^2 + a\sigma_{bc}^2 + c\sigma_{ab}^2 + \sigma_o^2$
Between C (SS)	c-1 = 1	78.125	78.125	$ab\sigma_c^2 + b\sigma_{ca}^2 + a\sigma_{ba}^2 + \sigma_o^2$
Between A (H_2O)	a-1 = 1	44.180	44.180	$cb\sigma_a^2 + c\sigma_{ab}^2 + b\sigma_{ca}^2 + \sigma_o^2$
B X C interaction	(b-1)(c-1) = 1	4.805	4.805	$a\sigma_{bc}^2 + \sigma_o^2$
C X A interaction	(c-1)(a-1) = 1	7.605	7.605	$b\sigma_{ca}^2 + \sigma_o^2$
A X B interaction	(a-1)(b-1) = 1	8.820	8.820	$c\sigma_{ab}^2 + \sigma_o^2$
Residual	(a-1)(b-1)(c-1) = 1	41.405	41.405	
TOTAL	(a-1)(b-1)(c-1) -1=0	202.940		

$$\frac{78.125*}{20.8025} = 3.76$$

$\therefore \sim 90\%$ significance

* Degrees of freedom (n_1) for 78.125 = 1
Degrees of freedom (n_2) for 20.8025 = 6

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"F-test" for variance ratio applied. The ratio is 3.76, corresponding to a significance level of 90 per cent. The 90 per cent level is reasonable for an analysis of variance on so few experiments. However, since the objective of the work was to find the conditions more likely to produce NF_2ClO_4, and not any high fluorine content mixture, the conclusion from the analysis of variance is of questionable value by itself.

In view of the fact that almost no solid product was formed in experiments with zero levels of all variables and that a phosphorous impurity was undesirable, it was decided to concentrate on experiments using water and metal as additives to the reactants. The question of catalytic activity by the metal surface still remained to be answered.

Eighteen such experiments were performed with a view to characterizing the product under these conditions. Results are found in Tables 29 and 30, the difference between the two tables being agitation of the reactor. In all cases, the product was a mixture of nitrosyl perchlorate and metal fluorides and there was no evidence for the presence of NF_2ClO_4. Table 35 shows the analyses of variance for the two series of experiments. The variability in the experimental results is obvious. It is also obvious that the 95 per cent confidence levels for the fluorine content are meaningless over such a wide range. What it does say is that the influence of unknown variables, or experimental error, is greater than that of the variables under study. It is interesting to note, however, that the standard deviation in the agitated reactions is somewhat less than that for the experiments that were not shaken. This is to be expected if the reaction were surface catalyzed. A few additional results with water and metal may be found in Table 31.

In addition to water, metal and P_2O_5, other materials were screened for catalytic acitivity. Table 28 lists these experiments. It is to be noted that copper turnings and hydrated ferric fluoride also were ineffective in producing anything other than $NOClO_4$ and metal fluorides.

Since one of the major difficulties encountered in characterization was the inability to achieve reproducible results from one experiment to another, the characterization program attempted to gain as much general information as possible about the various samples, and then to determine a complete material balance on a few selected ones. Since sample sizes were limited in many cases, not all techniques could be used on any one sample. Emphasis was placed on the characterization of non-phosphorus containing products.

In all cases the major product from the reaction of tetrafluoro-hydrazine with chlorine heptoxide was nitrosyl perchlorate. This was established by various methods:

(a) X-ray analysis showed the presence of powder patterns identical to those obtained for a standard $NOClO_4$ sample.

(b) elemental analyses gave nitrogen/chlorine ratios equal to that expected for $NOClO_4$.

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Table 35

Analysis of Variance

Table 30	Table 29
9.36	5.42
7.66	11.49
13.13	16.72
1.47	7.43
17.93	5.14
4.13	9.43
13.22	7.59
10.73	11.51
5.76	
11.42	9.34 (avg.)
9.48 (avg.)	

	Table 30	Table 29
ΣX^2	1112.88	801.59
(ΣX)	8988.94	5584.57
σ^2	23.78	14.79
σ	4.88	3.85
T%F	9.48 ± 9.76	9.34 ± 7.70

(c) titrations of the soluble portions of the product gave equivalent weights generally within 5 per cent of the theoretical value for $NOClO_4$. These titrations were conducted in aqueous solution, in nitromethane and in acetonitrile.

(d) quantitative infrared determination of the nitrosyl perchlorate content of that portion of the product soluble in acetonitrile was developed. Results were shown to be in agreement with the quantities suggested by equivalent weight determinations and material balances.

(e) fairly complete material balances for the entire product sample were obtained, which accounted for all the product on the basis of $NOClO_4$ being the only nitrogen containing constituent.

The remaining components in the mixture appeared to be metal fluorides. X-ray analysis showed the presence of iron (III) fluorides along with other unknown lines, some of which could be due to chromium and nickel fluorides, present from corrosion of the 304 stainless steel reactor. Some of these lines may also be due to the presence of complex metal fluoride such as $NiFeF_5$. The elemental analyses of the products gave ratios of metal to fluorine at the level expected for iron, nickel and chromium fluorides. In every case, all the fluorine could be accounted for as being combined with metal and there was never any "missing" fluorine that would cause one to suspect the presence of an N-F bond.

The problem of analyzing the product also was complicated by the lack of a suitable solvent, both for separation and for use in instrumental analysis. One major difficulty in determining whether the fluorine was bound to nitrogen or metal was the inability to employ NMR for these characterizations. The presence of the metal salts (particularly iron) prevented satisfactory signals from being obtained in the fluorine region. It was necessary therefore to prove or disprove the presence of NF containing materials by classical methods of separation and identification, where possible. The quantitative recovery and identification of the $NOClO_4$ from the product sample could not be achieved. No satisfactory solvent system was found in which the $NOClO_4$ could be dissolved from the remaining materials and then recovered quantitatively. In addition, the fluorides of some of the metals (most likely the metal complexes) were partially soluble in the solvents suitable for dissolving the $NOClO_4$. The instability of $NOClO_4$ was another problem resulting in the formation of yellow waxy products when attempts were made to evaporate solutions of the sample. This instability prevented quantitative recovery of $NOClO_4$ from solution. Sublimation of the product sample at $50°C$. and under pressures less than 10^{-4} mm. resulted in the formation of products which were non-condensable at room temperature.

The general procedure for characterization of the reaction products was to extract the product with nitromethane or acetonitrile and identify the components in both the insoluble and soluble portions. The insoluble residue was characterized by elemental analyses for flourine and metals. In reactions in which stainless steel filings were used as a catalyst, the insoluble portion contained free metal along with metal salts. The metal

was recovered by dissolving the sample in water and filtering. The metal cations were precipitated by base and the metal hydroxides were collected and ignited to metal oxides. In general, complete solution of $NOClO_4$ from the reaction product did not occur unless very large quantities of solvent were employed and the insoluble portion generally contained small amounts of non-extracted $NOClO_4$. This was identified by X-ray and infrared analyses.

The soluble portion was characterized by fluorine content and by the determination of equivalent weights. The hydrolysis of $NOClO_4$ results in the formation of two equivalents of acid for each mole of material. It was not possible to determine the exact products of the hydrolysis since apparently both nitric and nitrous acids formed. Analyses of standard samples of $NOClO_4$ showed the presence of two strong acids. Titration with permanganate generally indicated the presence of only 0.66 equivalents of an oxidizable material (NO_2^-), although the solutions had been previously flushed with nitrogen before hydrolysis. The expected hydrolysis would have given one equivalent of nitrous acid.

$$NOClO_4 + H_2O \longrightarrow HClO_4 + HNO_2$$
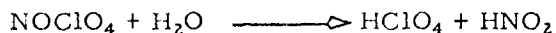
In any case, two equivalents of acid were formed and standard samples of $NOClO_4$ gave values of 67 for the equivalent weight (calcd; 64.8). The soluble portion of the product sample generally gave values of 70 when account was taken of the small amount of dissolved metal fluoride (or complex) that was present. It was not possible to determine the quantities of dissolved metal cations in the solution because of difficulty in obtaining quantitative precipitation when the solution was made basic. The complex metal salts apparently were quite stable under the conditions employed. For example, a positive test for ferric ion could not be obtained when the solution was tested with sodium thiocyanate. Upon prolonged standing in the presence of excess base, a precipitate finally did form which did give a positive color test for iron. In any case, the amount of metal fluoride, or complex, assumed to be present in the solution was determined by the actual fluorine content of the solution. This amount always agreed with that "missing" or unaccounted for in the insoluble fraction of the product sample.

Nitronium perchlorate, NO_2ClO_4, was not detected in any of the product samples. X-ray analyses and infrared scans of the product indicated the complete absence of this oxidizer. Extraction of a product sample with carbon tetrachloride (nitronium perchlorate forms approximately a 0.01 molar solution in carbon tetrachloride) followed by basic titration of the hydrolyzed filtrate showed the absence of any components. An infrared examination of the carbon tetrachloride solution used to conduct the reaction of N_2F_4 with Cl_2O_7 also showed the absence of NO_2ClO_4.

The procedure generally employed in obtaining a material balance is exemplified by the flow sheet in Figure 16 for sample NO. 3511-1. It is to be noted that in both the soluble and insoluble portions of the product, the ratio by weight of fluorine to metal is approximately unity. This is precisely what one would expect if the fluorides of iron, chromium and

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Figure 16

Flow Sheet for Material Balance

```
                    ┌─────────────────────┐
                    │ SAMPLE 3511-1       │
                    │ Wt.= 1.1605 g.      │
                    │ Metals = 0.1360 g.  │
                    └─────────────────────┘
                              │
                              │  Extract with Acetonitrile
                              │
            Residue          / \          Solution
                            /   \
                           ↓     ↓
              ┌─────────────┐   ┌─────────────┐
              │ 0.2754 g.   │   │ 0.8851 g.   │
              └─────────────┘   └─────────────┘
                    │                 │
        F = 0.0837 g.         F = 0.0524 g.
        Metals = 0.0846 g.    Metals = 0.1360 - 0.0846 =
                    │                      0.0514 g.
                    ↓                 ↓
           ┌──────────────┐   ┌──────────────┐
           │ 0.1071 g.    │   │ 0.7813 g.    │
           │ Base titration│   │ Eq. wt.      │
           │ gives Eq. wt. │   │ Found = 69   │
           │ of NOClO₄     │   │              │
           └──────────────┘   └──────────────┘
```
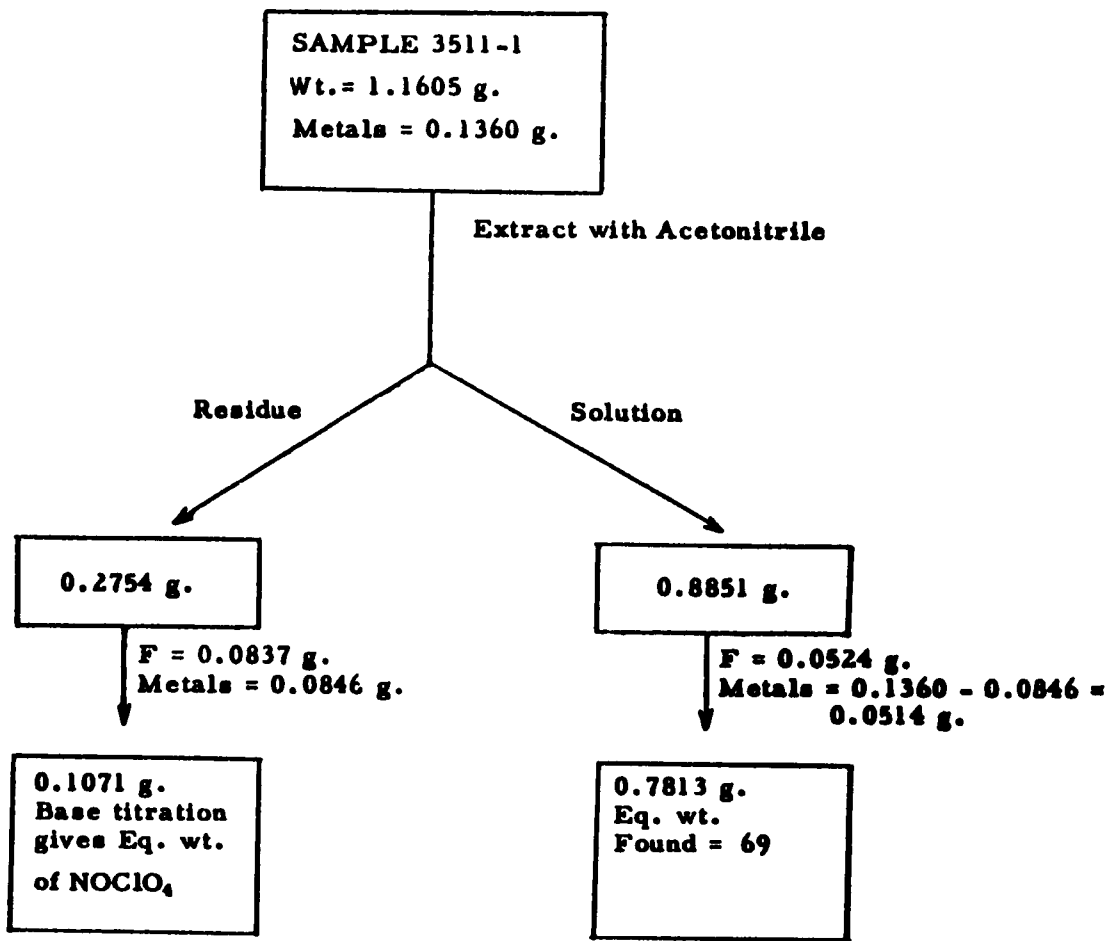
SUMMARY:

	$NOClO_4$	Metal Fluorides
	0.1071 g.	0.0837 g.
	0.7813	0.0846
	0.8884	0.0524
		0.0514
		0.2721

TOTAL: 0.0884 g.
           0.2721
           1.1605 g.

nickel were present in the same ratio in which these elements are normally found in 304 stainless steel.

Composition of 304 Stainless Steel

Fe	65-71%
Cr	18-20
Ni	8-12
Mn	2
Si	1

RATIO OF F/M

Calcd. for 304 Stainless Steel	Found in No. 3511-1
1.01	1.00

A summary of the analyses of several representative samples is given below:

Components	3511-1	Sample 1516-35 abc	1516-33
NOClO$_4$	0.8884 g.	0.4488 g.	0.6070 g.
F	0.1361	0.0959	0.1003
Metal(cation)	0.1360	0.0958	0.0958
Stainless steel	-	0.1773	0.2850
	1.1605 g.	0.8178 g.	0.0908 g.
Wt. of sample used	1.1605 g.	0.8178 g.	0.0938 g.

Preliminary evidence had already been obtained concerning the presence of phosphorus in the products. This early evidence was at first dismissed as simple contamination from the P_2O_5 used to prepared the Cl_2O_7.

$$6HClO_4 + P_2O_5 \longrightarrow 3Cl_2O_7 + 2H_3PO_4$$

The use of distilled Cl_2O_7 completely removed these impurities and products, not containing phosphorus, were prepared in this manner. When the presence of NF_2ClO_4 could not be demonstrated, however, it became of paramount importance to go back to the original reaction products (prepared from crude Cl_2O_7) and attempt to show the presence of NF_2ClO_4 among these.

Evidence had already been obtained that the introduction of P_2O_5 into the reaction mixture yielded products differing in composition from

those obtained when no P_2O_5 was present. This prompted a study of the "catalytic" activity of P_2O_5 (Table 28). It is to be noted that N_2F_4 does not react with P_2O_5, in the absence of Cl_2O_7, to yield any appreciable concentration of fluorine (Expt. 1528-57D). However, when Cl_2O_7 is present, fluorine contents of 13 to 15 per cent are achieved (Expts. 1516-17, 1738D-32 and -34), Table 28.

It soon became obvious that the phosphorus was not present merely as P_2O_5 and the compound $NOPF_6$ emerged as a likely contaminant. A procedure, utilizing infrared analysis was developed for the simultaneous quantitative determination of both $NOClO_4$ and $NOPF_6$ in the reaction mixtures.

The technique employed successfully for the identification and characterization of the non-phosphorus containing solid, was also applicable to the phosphorus containing material. This consisted of successive extractions with acetonitrile of the non-soluble portion of the reaction product. At the completion of the extraction, both the soluble and non-soluble portions were analyzed separately.

Simultaneous quantitative determination of both $NOClO_4$ and $NOPF_6$ involved an infrared analysis of solutions of the product in acetonitrile using a 0.084 mm. sodium chloride absorption cell. The $NOClO_4$, as ClO_4^- ion, is determined at 9.1μ and the $NOPF_6$, as PF_6^- ion, at 11.8μ. Calibration curves of absorbence vs. concentration were determined. A satisfactory Beer's Law plot was obtained from 0 to 0.55 absorbence units. Beyond this point, some deviation from Beer's Law was encountered. Copies of these plots are included as Figures 17 and 18. An example of a sample which was analyzed with the aid of quantitative infrared analysis is shown in Figure 19. Again, it is to be noted that a complete material balance was achieved and the ratio of fluoride to cationic metal was approximately unity, as would be expected.

The insoluble portion of the phosphorus containing product was most generally analyzed by elemental analysis for quantitative determination and X-ray for qualitative determination.

Flow sheets, with material balance data, outling the procedure for two typical samples are shown as Figures 20 and 21. The obtaining of a material balance, or fluorine balance, was used as the criteria for completed identification.

The components identified in the product resulting from the reaction of tetrafluorohydrazine with chlorine heptoxide in the presence of phosphorus containing material, such as P_2O_5, were nitrosyl perchlorate, nitrosyl hexafluorophosphate, and metal fluorides. No evidence was found for the presence of any N-F containing material.

Attempts were also made to repeat some of the earlier work on the reactions of Cl_2O_7 with N_2F_4 in which the products were noted to be extremely reactive (e.g., ability to etch glass) but these were not

Figure 17

NOClO$_4$ in Acetonitrile 9.1 μ

NaCl Cell--.084mm
1gm/100ml=1%

% NOClO$_4$ (Multiply by X purity Factor)

Absorbence
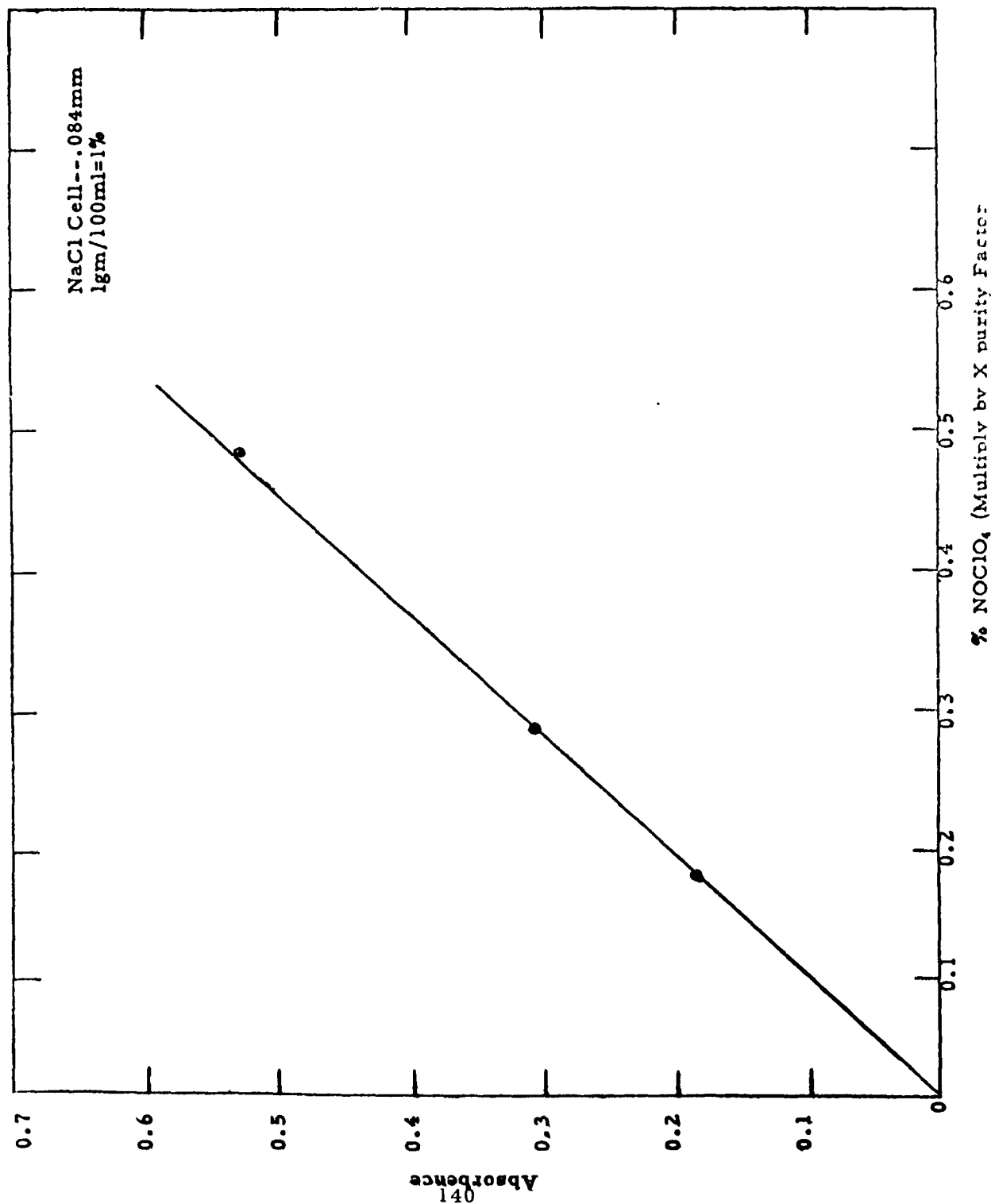
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Figure 18

NOPF$_6$ in Acetonitrile 11.8 μ

NaCl Cell-.084mm
1gm/100ml=1%

% NOPF$_6$ (Multiply by Y purity factor)
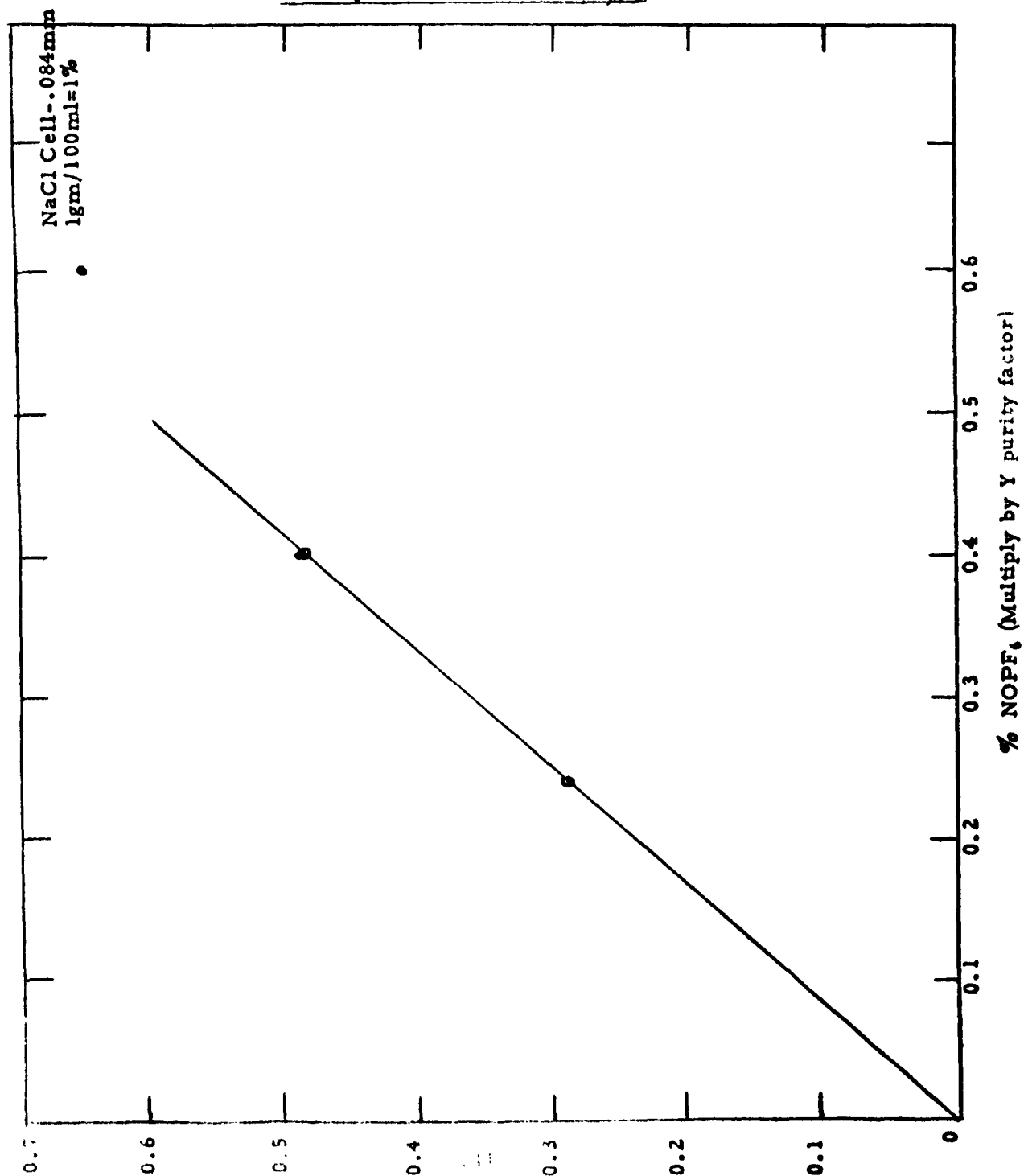
Figure 19

Analysis Via Infrared

```
┌─────────────────────────┐
│      SAMPLE  1516-35     │
│          a, b, c         │
│                          │
│    Wt. = 0.8178 g.       │
└─────────────────────────┘
              │
              │ Extract with Acetonitrile
              │
        ┌─────┴─────┐
   Residue         Solution
      │                 │
      ▼                 ▼
┌──────────┐      ┌──────────┐
│ 0.3350 g.│      │ 0.4828 g.│
└──────────┘      └──────────┘
```

F = 0.0646 g.
Metal (cation)=0.0643
Metal (S.Steel) = 0.1773

F = 0.0313g.
NOClO$_4$(via I.R.)=0.4200

```
┌──────────────┐      ┌──────────────┐
│ 0.0288 g.    │      │ 0.0315 g.    │
│ NOClO₄       │      │ Metal        │
└──────────────┘      └──────────────┘
```
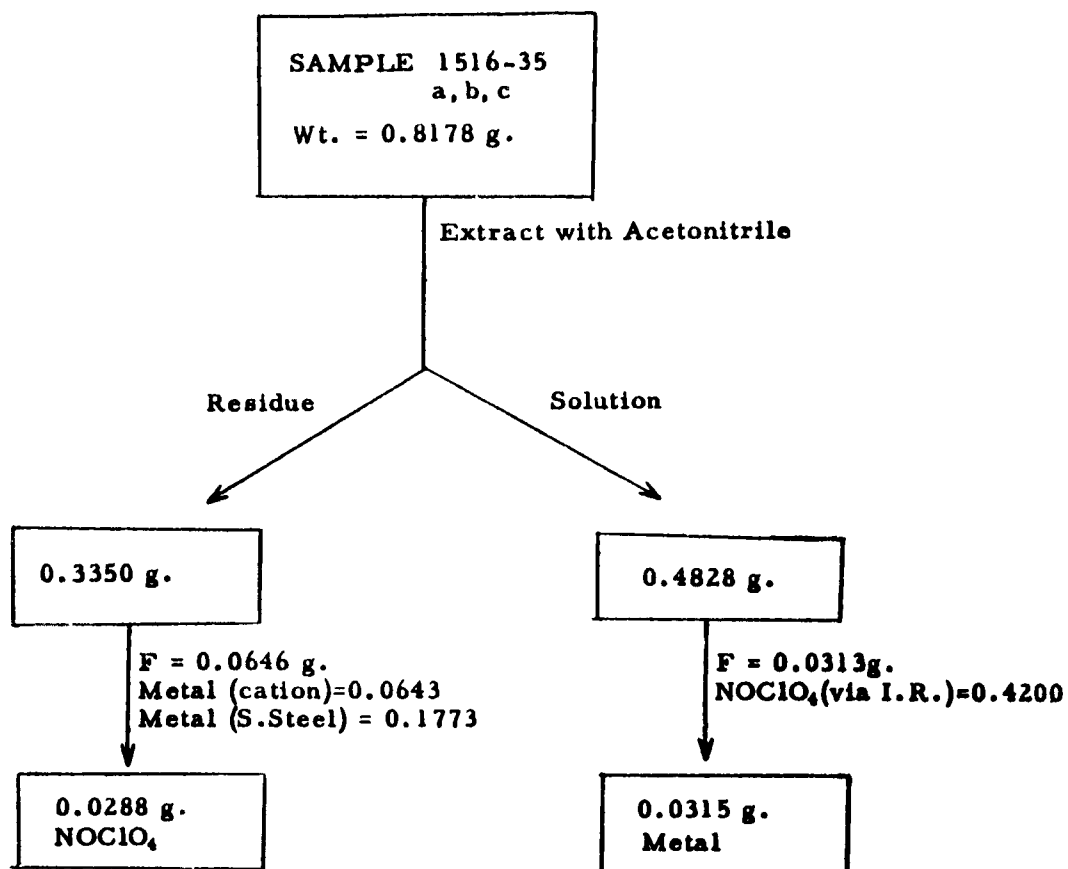
SUMMARY:	NOClO$_4$	Metal (cation)	Metal(S.Steel)	F
	0.4488 g.	0.0958 g.	0.1773 g.	0.0959 g.

TOTAL: 0.4488 g.
          0.0958
          0.1773
          0.0959
          ‾‾‾‾‾‾‾
          0.8178 g.

Figure 20

Material Balance Flow Sheet

1462-44-3
Wt. of sample
0.6875 g.

Soluble

Insoluble

25 ml. solution
of
Acetonitrile

Analyzed via IR
0.99% NOClO₄
0.84% NOPF₆

0.2475 g.
NOClO₄
0.2100 g.
NOPF₆

5.0 ml Aliquot
15.08 ml of 0.08 N
Base to Methyl
Red End Point

10 ml Aliquot
3.40 ml of
slight precipitate

0.2100 g.
0.4099
0.0310
0.0250
0.6759 g.

0.2184 g.
11.45% F

Metal = 0.031 g.
F = 0.025 g.
NOClO₄ = 0.1624 g.

Reextracted

Reextracted

0.0446 g.
of sample

Insoluble   Soluble

50 ml of
Acetonitrile
NOClO₄
0.0% NOPF₆

Metal
Fluoride

0.0124 g.

0.0742 g.

Soluble

Insoluble

>0.0169 g.
X-ray - Fe·F₃
present

10 ml of
Acetonitrile
NOClO₃

No
Fluorine

BALANCE:

NOPF₆   =
NOClO₄   =
Metal   =
Fluoride(as MF) =

% Acct. = $\frac{0.6759}{0.6825}$ x 100 = 98.3

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Figure 21

Fluorine Balance Flow Sheet

```
1580-21
0.4973 g. of
   sample
   F = 18.65
g. of F = 0.0926
```

Sample extracted with three
12 ml portions of Acetronitrile.
Portions combined and solution
increased to 50 ml.

Insoluble

```
0.076 g.
   F = 26.8
g. of F = 0.0204
```

Soluble

```
0.14  NOClO₄
0.22  NOPF₆
g. of F = 0.0715
```

BALANCE: F (as insoluble) = 0.0204 g.
          F (as soluble)   = 0.0715
                              ─────────
                              0.0919 g.

$$\% \text{Acct.} = \frac{0.0919}{0.0926} \times 100 = 99.24$$

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successful and phosphorus could be detected in the products. Infrared analysis of the acetonitrile solutions of two of these products showed $NOClO_4$ contents of 92.3 and 106.6%, respectively. The fluorine contents were below one per cent and no PF_6 ions could be detected in either sample.

Independent confirmation of our results was obtained by Dr. W. Friedlander and F. Fleming of Minnesota Mining and Manufacturing Co. (34). At our request, they examined one of our reaction products having the following contents: 23% F., 6.6% Fe and 4.67% P. X-ray definitely showed the presence of $NOClO_4$ and infrared examination indicated ClO_4^-, PF_6^-, covalent NO, a trace of $SiF_6^=$ and the complete absence of iron oxide and NO_2^+. If all the iron were present as FeF_3 and all the phosphorus as PF_6^-, the fluorine content of the sample would calculate to be 23.8%, in very good agreement with the found value of 23.0%. While this information, alone, is not sufficient to completely characterize the product, in conjunction with our quantitative separations and infrared studies, there appeared to be little doubt about the composition.

A comparison of products obtained both with and without phosphorus present showed that the only significant difference was the formation of $NOPF_6$. In both cases $NOClO_4$ and metal fluorides were formed.

The failure to obtain a product similar to the ones in which the presence of NF_2ClO_4 was first reported, emphasizes the inherent difficulties that are encountered in any reaction in which a reactive impurity is present in unknown concentrations. Since the amount of impurity may vary from experiment to experiment, the product composition and yield may also vary. Apparently, in the preparation of chlorine heptoxide with the use of the Waring Blendor, the amount of phosphorus pentoxide or phosphoric acid present as an impurity is dependent on a number of variables such as mixing rate, filtration rate, humidity, etc. Thus, it is possible to obtain pure or impure chlorine heptoxide depending on conditions.

On the basis of this general study the conclusion has been drawn that NF containing components were not present in the isolated reaction products.

It was concluded that:

1. Chlorine heptoxide does not react with tetrafluorohydrazine in carbon tetrachloride.

2. In the presence of metal and water, chlorine heptoxide reacts with tetrafluorohydrazine in carbon tetrachloride to form nitrosyl perchlorate and the corresponding metal fluoride.

3. There was no evidence for the formation of NF_2ClO_4 by the reaction of chlorine heptoxide with tetrafluorohydrazine in carbon tetrachloride.

b. Cl_2O_7 + NF_2H

Material

Cl_2O_7. Prepared as described above.

NF_2H. Prepared by the fluorination of urea as described in Section X.

Apparatus

The Teflon reactor is described in Figure 15. This reactor was attached to the high vacuum line described in Figure 14.

Procedure

In a nitrogen dry box a solution of chlorine heptoxide in carbon tetrachloride, or mixed solvent, was placed in the Teflon reactor containing a Teflon coated magnetic stirring bar. The reactor was attached to the vacuum line, cooled to -78°C. and the nitrogen pumped out. A measured amount of NF_2H was transferred to the reactor. The reactor was closed and then warmed to room temperature. The reactants were stirred for several hours at room temperature and then fractionated and analyzed.

Results

The objective of this study was to promote the following reaction:

$$ClO_3 - O - ClO_3 + NF_2H \xrightarrow[25°C.]{CCl_4} NF_2ClO_4 + HClO_3$$
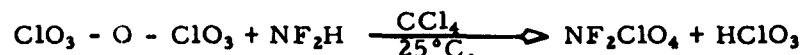
Ethyl Corporation (35) had studied the reaction in Pyrex apparatus at 250°C. and Thiokol, Reaction Motors Division (109), had reported a white solid forming in the absence of glass. It was our hope that, in the absence of glass and with pure reagents, we could demonstrate the formation and isolation of NF_2ClO_4.

A reaction did occur at 25°C. but the products were N_2F_4 and $NOClO_4$. The N_2F_4 was identified by infrared analysis of the volatile products. Nitrogen oxides also were detected. The small amount of solid product that precipitated from solution was identified as $NOClO_4$ by X-ray and infrared analyses.

There was no significant effect on the reaction course when solvents of high dielectric constant, nitromethane 39.4 or acetonitrile, 38.8, were used. When acetonitrile was used as the solvent no solid product formed. This could be due to the slight solubility of $NOClO_4$ in acetonitrile.

The results of this work, Table 36, were discouraging. There was no evidence for the desired product either in the solid or in the recovered solvents. The presence of nitrogen oxides in the off-gases indicated decomposition of the Cl_2O_7.

Table 36

Reactions of Chlorine Heptoxide

Expt. No.	Cl₂O₇ Wt.(g.)	Reactant	Reactant Wt. (g.)	Solvent (Ml.) CCl₄	CH₃CN	CH₃NO₂	Time Hrs.	Temp. (°C)	Results
2337D -40	2.59	HNF₂	1.33	50	-	-	2	-78 to 25	Infrared of off-gases: N₂F₄; Infrared of 0.78 g. solid: NOClO₄
-44	1.08	HNF₂	0.75	20	20	-	4	-78 to 25	Infrared of off-gases: N₂F₄; Infrared of solvent: ClO₄⁻; no solids obtained
-45	1.04	HNF₂	0.57	20	-	20	4	-78 to 25	Infrared of off-gases: possible N₂F₄; Infrared of solvent: only CCl₄, CH₃NO₂; Infrared of 0.497 g. solid: ClO₄⁻, some OH
-46	1.04	HNF₂	0.70	20	20	-	4	-78 to 25	Mass spectrometric analysis of off-gases: CCl₄, CH₃CN, N₂F₄, NO, N₂O, N₂; Mass Spec. anal. of solvent: CCl₄, CH₃CN; No solids obtained
-47	0.25	HNF₂	0.10	-	-	-	0.25	25	Infrared of gaseous mixture: NO₂
-43	1.35	NF₂Cl	0.77	50	-	-	4	-78 to 25	Infrared of solvent: Cl₂O₇, ClO₄⁻, NO₂; 0.072 g. solid product - no hydrolyzable fluorine

c. $Cl_2O_7 + NF_2Cl$

Material

Cl_2O_7. Prepared as described above.

NF_2Cl. Prepared by the reaction of NF_2H with sodium hypochlorite as described in Section X.

Apparatus

The Teflon reactor and vacuum line were those described previously (Figures 14 and 15).

Procedure

In a nitrogen atmosphere, a solution of chlorine heptoxide in carbon tetrachloride was added to the reactor. The reactor was closed, attached to the vacuum line, cooled to -78°C. and the nitrogen was pumped out. A measured amount of NF_2Cl was transferred to the reactor. The reactor was then warmed to 25°C. and the reactants were stirred with a Teflon coated magnetic stirring bar. After four hours, the product was fractionated and analyzed.

Results

This system was investigated to determine if NF_2ClO_3 could be prepared by the reaction

$$ClO_3-O-ClO_3 + NF_2Cl \longrightarrow NF_2ClO_3 + 2ClO_2$$

A reaction occurred but the desired compound was not detected in the products. Most of the Cl_2O_7 remained in the carbon tetrachloride and did not react. A trace of solid was obtained which did contain fluorine. The results, in general, however indicated that some decomposition of the reactants occurred by a complex mechanism, possibly involving traces of water or other impurities. The results are listed in Table 36.

B. Reactions with Cl_2O_6

1. Objective

Dichlorine hexoxide, a red liquid, is reported to be the least explosive of all the known oxides of chlorine. It does not explode with shock or sudden heat, although it may explode on contact with water or organic matter (37). Goodeve and Todd (38) showed that the oxide existed as ClO_3 radicals in the vapor phase, and the magnetic measurements of Farguharson, Goodeve, and Richardson (39) showed that in the solid and liquid phases, an equilibrium existed between the two forms:

$$Cl_2O_6 \rightleftharpoons 2ClO_3.$$

Schmeisser (42) found the Cl_2O_6 in the liquid phase reacts with various polar compounds to form perchlorates. On this basis he suggested that Cl_2O_6 can undergo self-ionization as follows:

$$Cl_2O_6 \rightleftharpoons 2ClO_3 \cdot \rightleftharpoons ClO_2ClO_4 \rightleftharpoons ClO_2^+ ClO_4^-$$
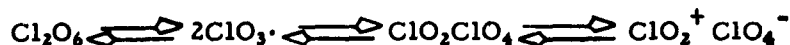
Since the paramagnetic monomer ClO_3 could easily be generated by vaporization of the liquid Cl_2O_6 and tetrafluorohydrazine can be dissociated to difluoramine radicals, the coupling reaction of ClO_3 with NF_2 was thought to be a feasible route to the synthesis of NF_2ClO_3.

In the liquid phase both Cl_2O_6 and N_2F_4 are in equilibrium with the respective paramagnetic form, therefore, a reaction was expected to occur, although slowly, to form the desired product. Reactions at low temperatures were preferred since the product NF_2ClO_3 was not expected to be very stable.

Both Cl_2O_6 and N_2F_4 are soluble in carbon tetrachloride and this fact made the use of Cl_2O_6 even a more attractive reagent for exploratory reactions.

Schmeisser's (42) work with Cl_2O_6 and reagents such as NOCl, HF and NO_2Cl also showed that reaction, _via_ ionic mechanism, may occur as follows:

$$ClO_2^+ClO_4^- + H^+F^- \longrightarrow HClO_4 + ClO_2F$$

$$ClO_2^+ClO_4^- + NO^+Cl^- \longrightarrow NO^+ClO_4^- + ClO_2 + 1/2Cl_2$$

$$ClO_2^+ClO_4^- + NO_2^+Cl^- \longrightarrow NO_2^+ClO_4^- + ClO_2 + 1/2Cl_2$$
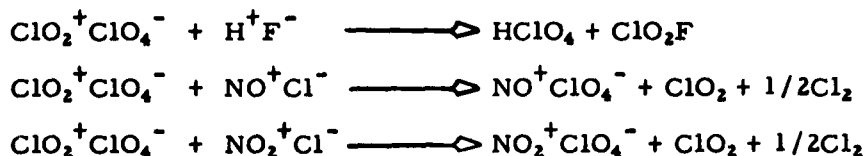
On this basis, it was hoped that analogous reactions with NF_2Cl or NF_2H might occur.

a. Cl_2O_6 + N_2F_4

Material

Cl_2O_6. Prepared by the reaction of ClO_2 with O_3 as described in Section X.

N_2F_4, E. I. DuPont de Nemours and Co. Purity 99%.

Apparatus

The apparatus used in liquid phase reactions of Cl_2O_6 with N_2F_4 is described in Figure 22. The apparatus designed for the reaction of NF_2 and ClO_3 radicals is described in Figure 23.

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Figure 22

Apparatus for Reaction of Cl_2O_6 with N_2F_4
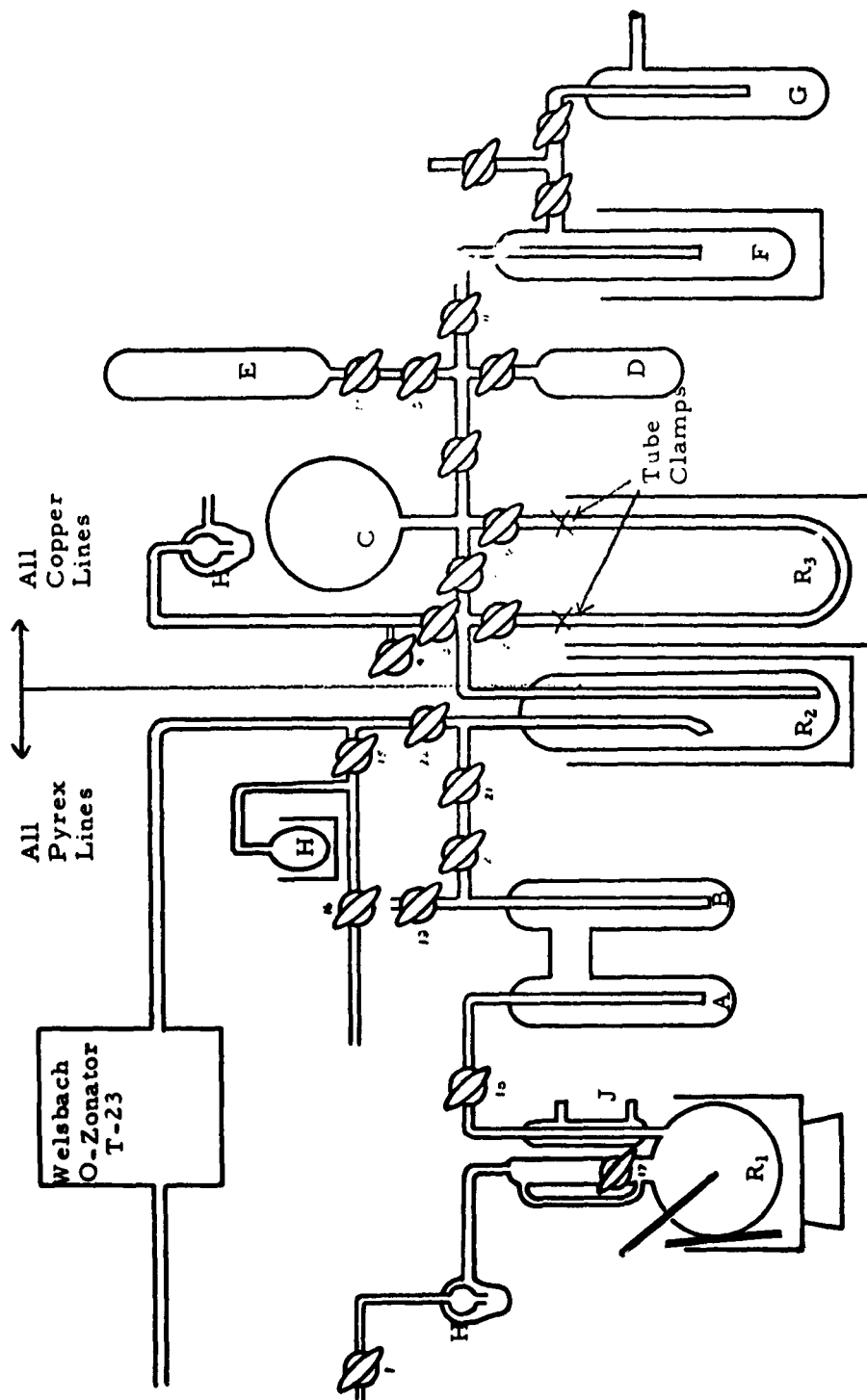
A. Drierite Column
B. P_2O_5 on glass beads
C. Vac. pressure gauge
D. 75 ml SS cylinder
E. N_2F_4 Cylinder
F. -196°C Pyrex trap

G. Soda and Lime trap
H. Kel-F oil bubble off
J. 0°C Condenser
R_1 50 ml Pyrex Reactor for prep ClO_2
R_2 Pyrex Reactor for prep Cl_2O_6
R_3 Teflon tube reactor for prep NF_2ClO_3

All Copper Lines

All Pyrex Lines

Tube Clamps

Welsbach O-Zonator T-23

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Figure 23 Reaction of NF$_2$ Radicals with ClO$_3$ Radicals

B: Conc. H$_2$SO$_4$
C: Drierite
D: P$_2$O$_5$ on glass beads
Darkened sections are teflon tubing

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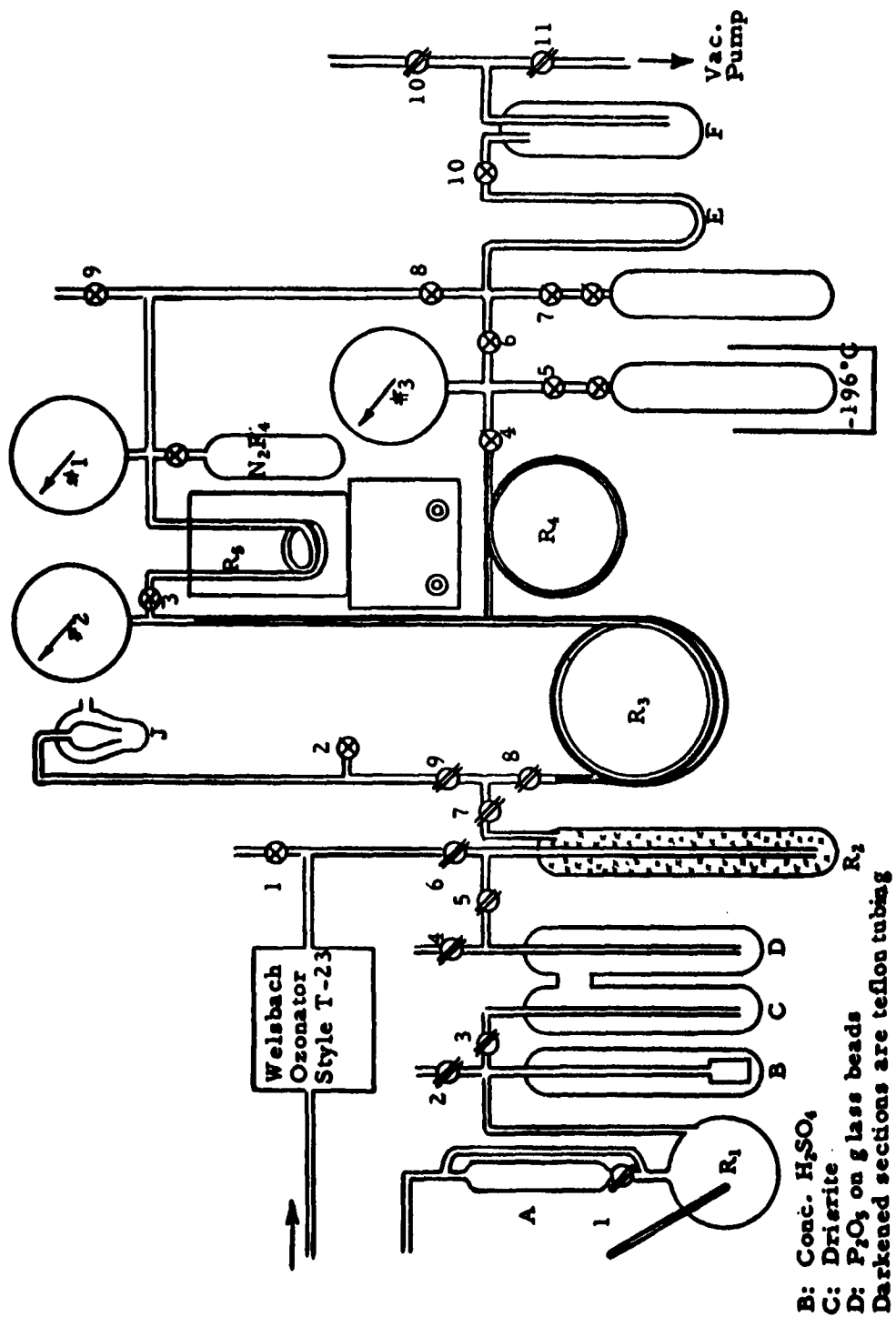
Procedure

Liquid Phase Reactions

In a typical experiment about one gram of Cl_2O_6 was distilled into the Teflon tube reactor R_3. In the initial experiments this Cl_2O_6 was not weighed since pure Cl_2O_6 was expected to decompose at 25°C. and, to avoid handling at 25°C., the amount of Cl_2O_6 added to the reactor was estimated. In later experiments when it was observed that Cl_2O_6 was quite stable in Teflon at 25°C. the Cl_2O_6 was weighed.

The Cl_2O_6 in R_3 was cooled to -196°C. and excess tetrafluorohydrazine was added to the reactor. The Teflon reactor was then isolated from the copper high vacuum line by collapsing the tube with tube clamps. The reactor was then warmed to the desired temperature and permitted to stand, generally for 16 hours. The product was then fractionated and analyzed.

Gas Phase Reactions

In a typical experiment about one gram of Cl_2O_6 was slowly distilled under vacuum from reactor R_3, Figure 23, through a Teflon "T" and condensed rapidly into reactor R_4 at -196°C. Simultaneously with the distillation of Cl_2O_6, N_2F_4 was passed through a heated copper coil R_5 (180°C.) and the resulting NF_2 radicals joined a stream of ClO_3 radicals in the Teflon "T" where reaction occurred. The products and/or reactants were quenched rapidly in the Teflon coil R_4 at -196°C. to prevent possible decomposition of unstable compounds. The products that collected in R_4 were then fractionated and analyzed.

Results

Experimental conditions and results of reactions in the liquid phase are summarized in Tables 37, 38, 39 and 40.

When N_2F_4 was added to liquid Cl_2O_6 in the absence of a solvent a slow reaction occurred, the red color of the Cl_2O_6 disappeared, and a small amount of solid formed. Gaseous products were also formed.

The white crystalline solid was identified by X-ray and infrared as $NOClO_4$. It was observed that the fluorine content of this solid product varied from a low of 0.6 to a high of 32.1 weight per cent. Since infrared analyses of the solid products did not show the presence of N-F bonds, it was suspected that the fluorine in these solid products was present in some undesirable form, possibly as HF from contamination. The elemental compositions for several possible products are shown on the following page.

Table 37

Reaction of Cl_2O_6 with N_2F_4

		1718-14	1718-32	1718-56
A.	**Experiment No.**	1718-14	1718-32	1718-56
B.	**Reactants**			
	Cl_2O_6(a)	0.5	0.5	1.0
	N_2F_4	1.2	1.2	5.7
C.	**Solid Product**			
	Amt. g. (a)	0.3	0.3	trace
	Analysis wt. %			
	F	32.1	0.6	13.2
	Cl	23.3	28.8	—
	N	—	1.8	—
	I.R. Analysis	$NOClO_4$	$NOClO_4$	—
D.	**Volatile Products**			
	Amt. Recovered (g.)	0.5	1.1	4.4
	I.R. Analysis	N_2F_4	N_2F_4	N_2F_4
			NOF trace	NOCl trace

Mass Spec. Analysis

mole %

H_2O	1.1	N_2O	0.9	N_2F_4	95.5
N_2	5.4	N_2	7.7	NO	4.5
N_2F_4	70.3	N_2F_4	75.8	N_2O	trace
NO	20.6	NOF	7.6		
HCl	2.5	O_2	8.0		

(a) Estimated-Since liquid Cl_2O_6 was considered too unstable for weighing at 25°C.

Table 38

Reaction of Cl_2O_6 With N_2F_4

	1805-3	1805-11	1805-20	1805-25	1805-34	1805-40
Reactants						
Cl_2O_6 (g.)	0.3 (a)	0.3 (a)	0.3 (a)	0.3 (a)	0.3 (a)	.654
N_2F_4 (g.)	0.466	0.506	1.166	0.5 (a)	0.859	0.5 (a)
Reaction Conditions						
T°C	-15	-15	-78	200	80	200
Reactor Type	Teflon	Teflon	Teflon	Teflon	Teflon	Teflon
Time (Hrs.)	12	12	60	2	2	1
Reactants Recovered						
N_2F_4 (g.)	.387	.243	.914	0	.750	0
Cl_2O_6 (g.)	-	-	-	0	-	0
Solid Product Composition	Unident.	NOClO4·XHF	NOClO4	NOClO4 +	NOClO4 +	NOClO4
Gaseous Product Composition	N2F4 NOF trace	N2F4 NOF trace NOCl trace	N2F4	NO2 ClO2 N2O	N2F4 NOF trace	N2O NF3 N2 NOCl

(a) estimated   Since Liq Cl_2O_2 was thought to be too unstable for weighing at 25°C.
— not determined

Table 39

Reaction of Cl_2O_6 with N_2F_4 in CCl_4 at 25°C.

Experiment No.	1718-62	1718-71	233D-79	233D-80	233D-82	233D-84	1718-75	1718-80
Reactants								
Cl_2O_6 (g) (b)	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5
N_2F_4 (g)	1.0	–	–	1.2	0.6	1.1	0.6	1.3
CCl_4 (g)	32.0	32.0	32.0	32.0	32.0	32.0	32.0	32.0
Solid Product								
Amt. (g)	0.1[a]	0.5[a]	trace[a]	0.2	0.1[a]	0.1[a]	0.9	0.1[a]
Analysis wt.								
F	29.1	15.3	10.3	2.5	2.2	2.7	11.9	22.8
Cl	22.5	34.5	–	28.7	29.8	28.0	31.4	32.9
N	9.5	11.1	–	8.4	–	9.8	8.8	10.8
I.R. Analysis	$NOClO_4$	–	–	–	–	$NOClO_4$	–	–
Volatile Products								
Amt. Recovered	–	–	–	0.8	–	–		
I.R. Analysis	N_2F_4 only	–	–		–	–	N_2F_4 NOF trace NO_2 trace	N_2F_4

[a] Estimated

b wt. was estimated since liquid Cl_2O_6 was thought to be too unstable for weighing at 25°C.

Table 40

Reaction of Cl_2O_6 with N_2F_4

	1805-67	1805-80
Reactants		
Cl_2O_6	0.223	1.988
N_2F_4	0.301	1.771
Reaction Conditions		
T°C	150	40-45°C 150
Reactor Type	Teflon (no metal)	Teflon (Exposed Metal Press. Gauge)
Time, Hrs.	0.5	19.5 (40-45°C) 0.5 (150°C)
Reactants Recovered		
Cl_2O_6	None	None
N_2F_4	0.183	None
Solid Prod. (g.)	0.113	0.258
Analysis IR	$NOClO_4$, NO_2ClO_4	$NOClO_4$, NO_2ClO_4
X-ray	$NOClO_4$	$NOClO_4$
Gaseous Prod., Wt. g.	0.204	1.654
Composition	N_2F_4, NOF, NCl, CO_2 O_2	NF_3, NOCl, NO2, N2O CLO_2
Liquid Prod. Analysis	0.095 Inconclusive	None Considerable attack on metal vacuum lines occurred to form metal fluorides.

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Compound	Theory		
	F	Cl	N
NF_2ClO_3	28.0	26.0	10.3
$NOClO_4$	0.0	27.4	10.8
$NOClO_4 \cdot HF$	12.7	23.7	9.4
$NOClO_4 \cdot HF$	22.2	20.9	8.3
$NOClO_4 \cdot 3HF$	30.1	18.7	7.4
1718-62 (found Table 39)	29.1	22.5	9.5

While the composition of some of the solid products, such as 1718-62, approximated the theoretical composition for NF_2ClO_3, the fluorine content varied over a wide range for products obtained from identical experiments. The fact that both infrared and X-ray analyses also identified $NOClO_4$ as the major component was not encouraging. However, the presence of fluorine was not consistent with the X-ray and infrared analyses.

To determine whether HF was present in the solid, the product prepared in Experiment 1718-80, Table 39, was analyzed.

		Found	Theoretical for NF_2ClO_3
Wt. %	F	22.8	28.0
	Cl	32.9	26.1
	N	10.8	10.3

Since the product was prepared by the reaction of Cl_2O_6 with N_2F_4 in carbon tetrachloride, the high chlorine value was attributed to a small amount of absorbed carbon tetrachloride.

Infrared analysis of this solid showed the characteristic bands for $NOClO_4$. A weak band was also noted at 2.7μ which is in the region where HF would show an aborption band.

To confirm the presence of HF, a sample of this solid product was heated to 130°C. for 2 hours in the presence of very pure NaF in a closed all-Teflon tube reactor. The objective was to promote the following decomposition reaction:

$$2NOClO_4 \cdot 2HF + 4NaF \xrightarrow{130°C.} 4NaF \cdot HF + 2ClO_2 + 2NO_2 + O_2$$

The formation of $NaF \cdot HF$ was confirmed by X-ray and infrared analyses. X-ray analysis of the starting NaF showed no bifluoride.

It was also observed that the fluorine could be removed from various solid products by subjecting the products to high vacuum with

continuous pumping.

On the basis of this data it was concluded that the solid products obtained by the liquid phase reaction of Cl_2O_6 with N_2F_4 alone, or in carbon tetrachloride, consisted of $NOClO_4$ and varying amounts of additional HF. The source of the hydrogen containing component could not be established. The gaseous products consisted of N_2F_4, NOF, ClO_2, NO_2, N_2O and NF_3. There was no evidence for NF_2ClO_3 in the gaseous products or in the carbon tetrachloride when the solvent was used.

The experimental conditions and results of vapor phase reactions are listed in Tables 41 and 42.

Reactions with NF_2 and ClO_3 radicals were faster than the liquid phase reactions with Cl_2O_6 and N_2F_4. The major solid products of the vapor phase reactions were nitrosyl perchlorate and nitronium perchlorate, and the gaseous products generally consisted of NOF, NOCl, NO_2Cl, NO_2, N_2O, NF_3 and ClO_2.

The main reaction appeared to be oxidation of NF_2 radicals with the formation of nitrogen oxides and NOF which then react further to produce the nitrosyl and nitronium perchlorates.

The transitory existence of the desired product NF_2ClO_3 cannot be ruled out, but if this compound formed, all attempts to isolate it or detect its presence in crude products at low temperature were unsuccessful.

The product composition indicated that the reaction of ClO_3 with NF_2 radicals is complex due to the interaction of products and the decomposition of the more unstable species. A possible sequence leading to the products found is:

$$N_2F_4 \rightleftharpoons 2NF_2\cdot$$

$$Cl_2O_6 \rightleftharpoons 2ClO_3\cdot$$

$$NF_2\cdot + ClO_3 \longrightarrow NF_2ClO_3 \longrightarrow NOF + NO_2 + NO + ClO_2$$

$$NOF + Cl_2O_6 \longrightarrow NOClO_4 + ClO_2F$$

$$NO_2 + Cl_2O_6 \longrightarrow NO_2ClO_4 + ClO_2$$

$$NF_2 + ClO_2F \longrightarrow NF_3 + ClO_2$$

$$NF_2 + ClO_2 \longrightarrow NOCl + NO_2Cl + NOF + NO_2$$
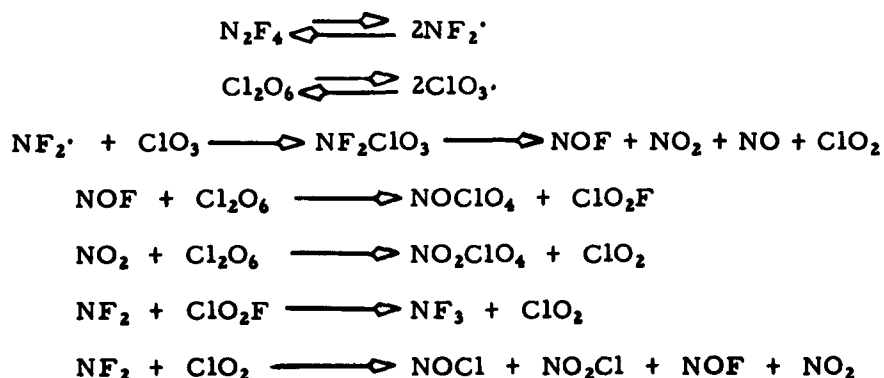
The absence of ClO_2F in the gaseous products and the presence of only traces of ClO_2 were attributed to the reactivity of these materials.

In experiments 1943-25 and 1943-47, an unidentified liquid was detected. This liquid was not noticed in any of the products from the liquid phase reactions of Cl_2O_6 with N_2F_4. It was hoped that this liquid might be

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Table 41

Reaction of NF₂ and ClO₃ Radicals

Experiment No.	1943-25	1943-40	1943-47
I Reactants			
ClO₄ (g.)	1.546	0.720	1.141
N₂F₄ (g.)	4.678	2.850	3.467
	6.224	3.570	4.608
II Experimental Conditions			
Reactor Type	Teflon "T"	Teflon "T"	Teflon "T"
Reactor Vol (ml.)	5	5	5
T°C N₂F₄	175	170-180	175
T°C ClO₄	25	25	33
Reactant Residence Time (sec.)	0.0158	0.0155	0.0122
T°C Product Trap	-196 (Teflon)	-196 (Teflon)	-196 (Monel)
Reaction Time (min.)	35	30	12
Pressure (mm Hg)	3	2	5
III Products			
Fraction Volatile at -140°C	4.390	2.790	3.353
Fraction Volatile at -78°C	0.513	0.398	0.482
Fraction Volatile at RT	0.590	0.367	0.404
Fraction Solid at RT	0.232	Trace	0.399
	5.725	3.555	4.638
IV % Material Recovered	92.0	99.6	100.6
V Product Identification			
Fraction Volatile at -140°C	N₂F₄, Trace, NF₃, NOF	N₂F₄, Traces NOF, NF₃, NOCl, NO₂	N₂F₄, NF₃, N₂, NO
Fraction Volatile at -78°C	HNO₃, Unidentified Compound	HNO₃, NO₂Cl	HNO₃, Unidentified Compound
Fraction Volatile at RT	N₂O, NO, NOCl	NOCl, NO₂	NOCl, NO₂
Fraction Solid at RT	NOClO₄, with F=0.50	Discarded	NOClO₄

Table 42

Reaction of NF_2 and ClO_3 Radicals

	Exp. 1891-3	Exp. 1891-18
Reactants		
Cl_2O_6 (g.)	0.809	2.202
N_2F_4 (g.)	1.320	2.557
	2.129	4.759
Reaction Conditions		
Time (min.)	81	107
Temp. ^oC	25	25
Flow rate Cl_2O_6	1.3 ml./min.	2.8 ml./min.
Flow rate N_2F_4	3.5 ml./min.	5.2 ml./min.
Pressure mm. Hg.	3	3
Product Fractions		
Volatile at -130^oC	0.535	2.183
Volatile at -78^oC	0.784	0.038
Volatile at -30^oC	0.090	0.225
Liq. at 25^oC	0.094	1.862**
Solid at 25^oC	0.626*	0.403
Volatile at 0^oC	0.000	0.048
	2.129	4.759

Net Product Composition

	Exp. 1891-3		Exp. 1891-18
N_2F_4	1.076	N_2F_4	2.183
NOF	0.118	ClO_2	0.311
NF_3	0.020	Cl_2O_6	1.862
CL_2	0.016	$NOClO_4$	0.403
HCl	0.027		4.759
CO_2	0.005		
N_2	0.027		
$NOClO_4$	0.656		
Cl_2O_6	0.094		
NO_2	0.090		
	2.129		

* Only 0.226 g. of solid was collected, but more solid was visible on the reactor walls and could not be collected.

** 1.134 g. Liquid was collected. Additional liquid is on hand (about .5 g.) but not weighed.

the desired NF_2ClO_3 since crude samples liberated HF on hydrolysis. However, when this unidentified product was carefully fractionated and then analyzed by infrared, the simplified spectra using silver chloride windows in a 5 centimeter stainless steel cell was obviously not due to NF_2ClO_3. The unknown was thought to be a nitrate although not fluorine nitrate. A literature search revealed that the infrared spectrum of chlorine nitrate published by Brändle, Schmeisser and Lüttke (40), was similar to the spectrum of the unidentified product. Brändle, Schmeisser and Lüttke used sodium chloride windows for the infrared analysis of chlorine nitrate and some interaction with the windows occurred. The fundamental absorption frequences of chlorine nitrate, excluding the bands due to interaction with sodium chloride windows, were identical to the unknown product. The infrared spectrum is shown in Figure 24.

The molecular weight of this product was determined by the usual P-V-T relationship:

Found: 97.9 g./mole
Theoretical for $ClNO_3$: 97.5 g./mole

On this basis of the infrared spectra and molecular weight, the unknown was identified as $ClNO_3$.

This same product was prepared by investigators at General Electric by the reaction of NF_2Cl with OF_2 in an electric discharge (41). In this case a similar reaction resulting in oxidation of the NF_2Cl could produce $ClNO_3$. The infrared spectra of the unidentified product "Compound B" prepared by General Electric is shown in Figure 25.

It was concluded that gas phase reactions of NF_2 and ClO_3 radicals result in the oxidation of the NF_2 radical and, if NF_2ClO_3 is formed, it must decompose readily. Isolation of this compound would require special techniques.

The apparatus described in Figure 23 was modified in an attempt to detect the presence of NF_2ClO_3 in the crude products of the reaction of ClO_3 with NF_2 radical by low temperature NMR. The modified apparatus is depicted in Figure 26.

Streams of NF_2 and ClO_3 radicals were generated and quenched directly into a Teflon NMR tube at -196°C. The NMR tube containing the product was then placed in an NMR F^{19} probe precooled to -196°C. and warmed slowly to room temperature with constant field scanning.

The objective was to detect the presence of NF_2ClO_3 in the crude product by fluorine resonance signals. If NF_2ClO_3 were present, a chemical shift due to N-F bonding was expected.

Only N_2F_4 (chemical shift-55 PPM relative to Freon-11) was detected. Since excess N_2F_4 was used this was the strongest fluorine signal detected. Decomposition products of NF_2ClO_3 were not detected possibly due to low concentration of these products in excess N_2F_4.

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Figure 24

Infrared Spectrum of Reaction Product from $ClO_3 \cdot$ and $NF_2 \cdot$
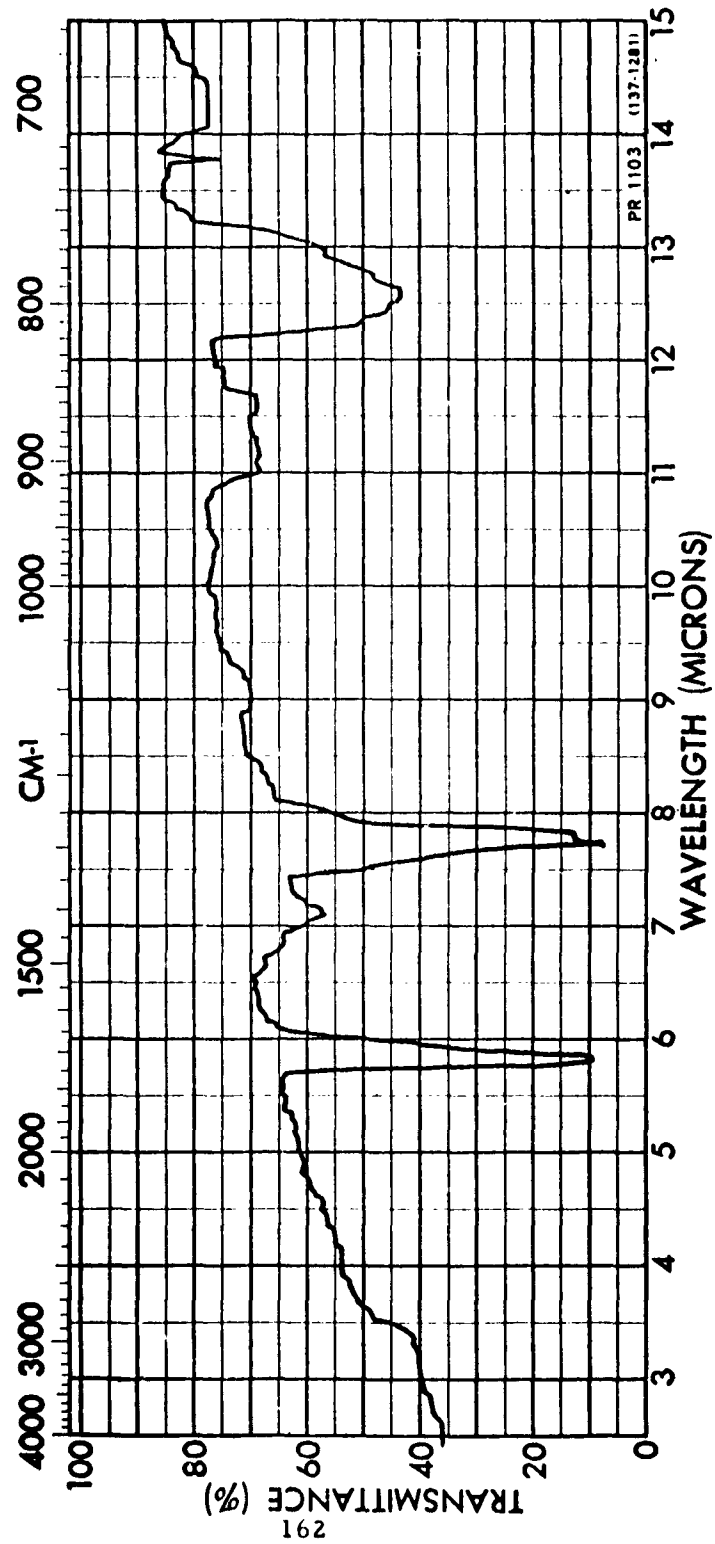
Figure 25

PRODUCT FROM REACTION OF OF_2 + NF_2Cl

General Electric Co., Development of High Energy,

Storable Liquid Propellant Systems, Final Report

Contract AF 04(611) 7412, May 1962

163
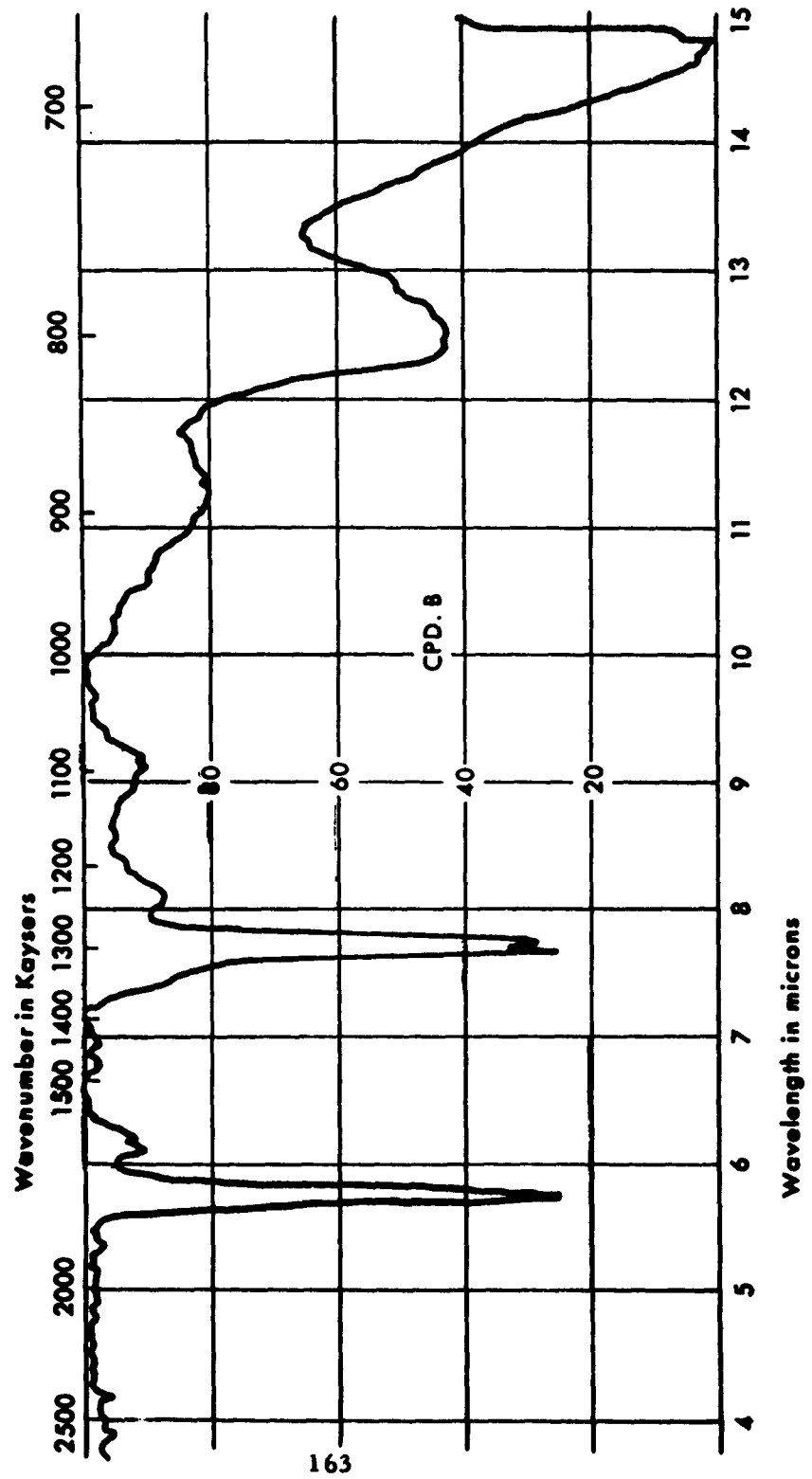
Figure 26

Modified Apparatus for Reaction of NF_2 + ClO_3 Radicals

Pressure gauge

Pressure gauge

Teflon "T"

Teflon tube

NF_2

N_2F_4

Vacuum pump

ClO_3

by pass valve

Aluminum valve

Cl_2O_6

N_2F_4

Teflon NMR Tube

NF_2ClO_3

Hot oil bath

—196 °C bath
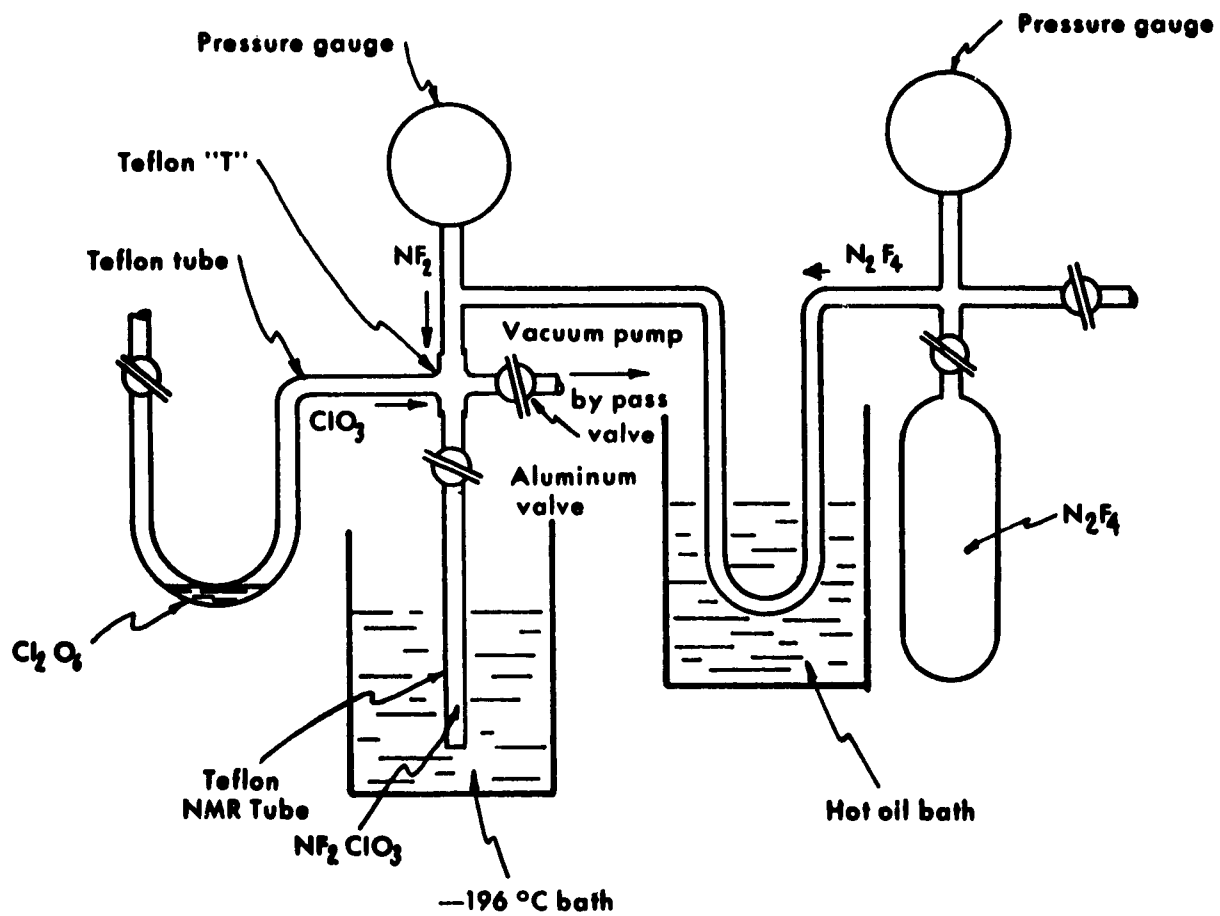
Poor thermal conductivity of the Teflon apparently hindered rapid quenching of the products.

b. Cl_2O_6 + NF_2H

Material

Cl_2O_6. Prepared as described above.

NF_2H. Prepared by the reaction of thiophenol with N_2F_4. Mass spectrometric analysis showed the NF_2H to contain considerable impurities.

	Material A	Material B
NF_2H	12. 9 mole%	64. 1 mole %
CO_2	82.4	32.8
N_2O	3.4	0.0
N_2F_4	1.3	3.1
	100.0	100.0

Apparatus

The apparatus is described in Figure 23.

Procedure

In a typical experiment approximately 0. 5 g. of Cl_2O_6 was distilled into the Teflon tube reactor R_4, Figure 23. The reactor was cooled to -196°C. and 0.5 g. of NF_2H was condensed into R_4. The reactor was then closed by collapsing the tube with a tube clamp to isolate the reactants from the copper components of the vacuum line. The reactants were warmed to 0°C. and held there for 12 to 60 hours. Periodically the reactor was opened to pressure gauge No. 3 to note pressure changes due to reaction. The product was then fractionated and analyzed.

Results

Schmeisser (42) had investigated the reaction of Cl_2O_6 with a variety of reagents. He observed that the products of the reactions were those expected for Cl_2O_6 existing in the form $ClO_2^+ClO_4^-$. Schmeisser obtained the following results with hydrogen fluoride:

$$H^+F^- + ClO_2^+ClO_4^- \longrightarrow HClO_4 + ClO_2F$$

On this basis and other analogous reactions, it was reasonable to propose the possible formation of ClO_2NF_2 from difluoramine and dichlorine hexoxide:

$$H^+NF_2^- + ClO_2^+ClO_4^- \longrightarrow HClO_4 + ClO_2NF_2$$
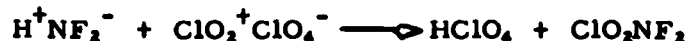
The results of two experiments are listed in Table 43.

Table 43

Reaction of Cl_2O_6 With HNF_2

Reactants	1805-49	1805-59
Cl_2O_6 (g.)	0.3 (a)	.60
NF_2H (g.)	0.45	0.47
Reaction Conditions		
T°C	0	0
Reactor type	Teflon	Teflon
Hrs.	60	12
Reactants Recovered		
NF_2H (g.)	0	0.5 (a)
Cl_2O_6 (g.)	0	0
Solid Product Composition	$NOClO_4$	$NOClO_4$
Liquid Product Composition	Unidentified	$NOF \cdot 3HF$
Gaseous Product Composition	CO_2	-
	$NOCl$	-
	N_2	-

(a) estimated.

In experiment 1805-49, material A, the gas mixture containing only 12.9 mole per cent NF_2H, was reacted with Cl_2O_6. When the gas was added to the Cl_2O_6 and held at 0°C., the pressure dropped and both difluoramine and tetrafluorohydrazine were found to be absent when the product gas was analyzed by infrared. The composition was 70.8% CO_2, 9.3% NOCl and 19.9% N_2. The material remaining was a mixture of a white solid and a volatile pale yellow liquid. The solid was identified by infrared and X-ray as $NOClO_4$.

	Found	Theor. $NOClO_4$
F	1.3%	0%
Cl	30.4	27.4
N	9.5	10.8

The liquid melted at -5 to 0°C. but further characterization could not be completed because of the limited sample size.

In experiment 1805-59, the purer difluoramine (material B) was employed. As observed above, the addition of HNF_2 to Cl_2O_6 led to a pressure decrease. After 12 hours a leak developed in the reactor and the experiment was terminated early. The unreacted Cl_2O_6 was removed by decantation (tends to coalesce similar to mercury) leaving a solid and liquid product. The liquid was distilled into a Teflon tube and approximately 0.5 ml. of pale yellow material was obtained.

A portion of the liquid was dissolved in CCl_4 and examined by infrared. Weak bands at 5.4, 5.5μ and a very strong band at 8.9μ were evident. Elemental analysis of the liquid showed the following:

	Found	Theor. NOF·3HF
F	67%	69.7%
N	11.6	12.8
Cl	Less than 1	0.0

The reaction of HNF_2 with Cl_2O_6 is relatively slow but leads to the complete disappearance of the HNF_2 and the formation of a solid and liquid product. The solid is almost entirely $NOClO_4$. The liquid contains less than one per cent chlorine and has fluorine and nitrogen contents close to that predicted for NOF·3HF. The infrared bands at 5.4 and 5.5μ are consistent with the absorptions reported by Seel (43) for NOF·3HF. An additional strong band at 8.9μ, however, could not be assigned. On the basis of the evidence it was concluded that the reaction of Cl_2O_6 with HNF_2 results in oxidation and the products isolated are the result of secondary reactions. One possible scheme which can be proposed to explain the

pressure drop and the formation of both $NOClO_4$ and $NOF \cdot 3HF$ is presented below:

$$Cl_2O_6 \rightleftharpoons 2ClO_3$$

$$\left\{ \begin{array}{l} ClO_3 + HNF_2 \longrightarrow ClO_2 + HF + NOF \\[1em] ClO_2 + HNF_2 \longrightarrow ClO + HF + NOF \\[1em] ClO + HNF_2 \longrightarrow 1/2\, Cl_2 + HF + NOF \end{array} \right.$$

$$NOF + ClO_2ClO_4 \longrightarrow NOClO_4 + ClO_2F$$

$$NOF + 3HF \longrightarrow NOF \cdot 3HF$$
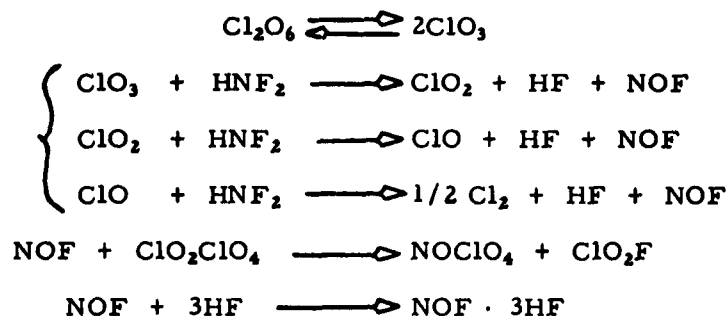
Chlorine and chloryl fluoride were not identified but it is doubtful that the concentration of these products would have been sufficient to be detected.

c. $Cl_2O_6 + NF_2Cl$
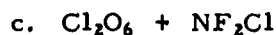
Material

Cl_2O_6. Prepared as described.

NF_2Cl. Prepared by the reaction of NF_2H with $NaOCl$. Purity: 98% NF_2Cl, 2% N_2F_4.

Apparatus

The apparatus is described in Figure 23. This system was modified slightly. Reactor R_4 was removed and the reaction was conducted in the Teflon tube reactor R_3.

Procedure

The Cl_2O_6 (1.059 g.) was distilled into reactor R_3 at -78°C. The reactor was then warmed to 0°C., pressured with NF_2Cl(0.778 g.), closed and held for 2-1/2 hours at 25°C. Since the pressure of Cl_2O_6, a blood red liquid, visible through the walls of the thin walled Teflon tube, showed no change, the reactants were heated to 100°C. for 15 minutes. At 100°C. the Cl_2O_6 either reacted or decomposed, although not completely. The products were then fractionated and analyzed.

Results

The results are summarized in Table 44.

The objective of this experiment was to prepare NF_2ClO_4. In the liquid phase, reaction of $NOCl$ with Cl_2O_6 proceeds to yield a perchlorate.

$$ClO_2^+ClO_4^- + NO^+Cl^- \longrightarrow NOClO_4 + ClO_3 + 1/2Cl_2$$

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Table 44

Reaction of Cl_2O_6 + NF_2Cl

Experiment No.   1943-12

I.   **Reactants**

Cl_2O_6 1.059 g.

NF_2Cl 0.778 g.
                                        _____
                                        1.837 g.

II. **Experiment Conditions**

T°C.   25°C. 2 1/2 hrs., 100°C. 1/4 hr.

Time (hrs.)   2 3/4 hrs.

Reactor Type   Teflon (open to metal pressure gauge)

III. **Products**

Solid at 25°C.   0.252 g.

Liquid at 25°C.   0.647 g.

Gas at 25°C.   0.532 g.
                                        _____
                                        1.431 g.

IV. **Product Identification**

Solid at 25°C. $NOClO_4$ by Infrared and X-ray

			Found	Theo. for $NOClO_4$
wt. %	F		1.63, 0.53	0.0
	Cl		29.5	27.4
	N		—	10.8

Liquid at 25°C. Cl_2O_6 by Infrared

Gas at 25°C. ClO_3F, NOCl, N_2F_4

V.   **Material Accounted for**   77%

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An analogous reaction with NF_2Cl would be

$$ClO_2^+ ClO_4^- + NF_2^{3+} Cl^{-3} \longrightarrow NF_2ClO_4 + ClO_2 + 1/2Cl_2$$

A reaction occurred between Cl_2O_6 and NF_2Cl to yield primarily $NOClO_4$ and ClO_3F. All of the NF_2Cl was converted to ClO_2F, $NOCl$, and N_2F_4 but approximately 80 per cent of the Cl_2O_6 was recovered. The solid product was identified by X-ray and infrared analyses. Elemental analysis of the solid showed

Wt. %		Found	Theor. for $NOClO_4$
	F	1.63, 0.53	0.0
	Cl	29.5	27.4
	N	-	10.8

The presence of substantial concentrations of $FClO_3$ in the product indicates that Cl_2O_6 was fluorinated by some complex mechanism resulting in decomposition of the NF_2 group. There was no evidence for the formation or the presence of NF_2ClO_4 in the products.

C. Reactions with ClO_2

1. Objective

Chlorine dioxide, like most so called odd molecules, is a very reactive substance. The explosive tendency of pure gaseous chlorine dioxide limited its use in many reactions but if the gas is diluted with air or CO_2, it can be handled safely.

It was hoped that if ClO_2 was diluted with tetrafluoro-hydrazine in the vapor phase, a reaction would occur to form a new compound NF_2ClO_2. Schmitz and Shumacher (44) showed that the controlled reaction of fluorine and chlorine dioxide results in the formation of a compound $FClO_2$ with a covalently bonded fluorine atom. A similar reaction was expected to occur with tetrafluorohydrazine.

a. $ClO_2 + N_2F_4$

Material

ClO_2. The chlorine dioxide was prepared by the reaction of Cl_2 with $NaClO_2$.

$$Cl_2 + 2NaClO_2 \xrightarrow{N_2} 2ClO_2 + 2NaCl$$

N_2F_4. Stauffer Chemical Co., Chauncy, New York. Purity 87.7%

Apparatus

The apparatus is described in Figure 27. Because of the explosive nature of chlorine dioxide the system was provided with several traps, expansion bulbs and a vent to facilitate the safe handling of the ClO_2. The

Figure 27

Combination ClO$_2$ Generator and Reactor for ClO$_2$ + N$_2$F$_4$
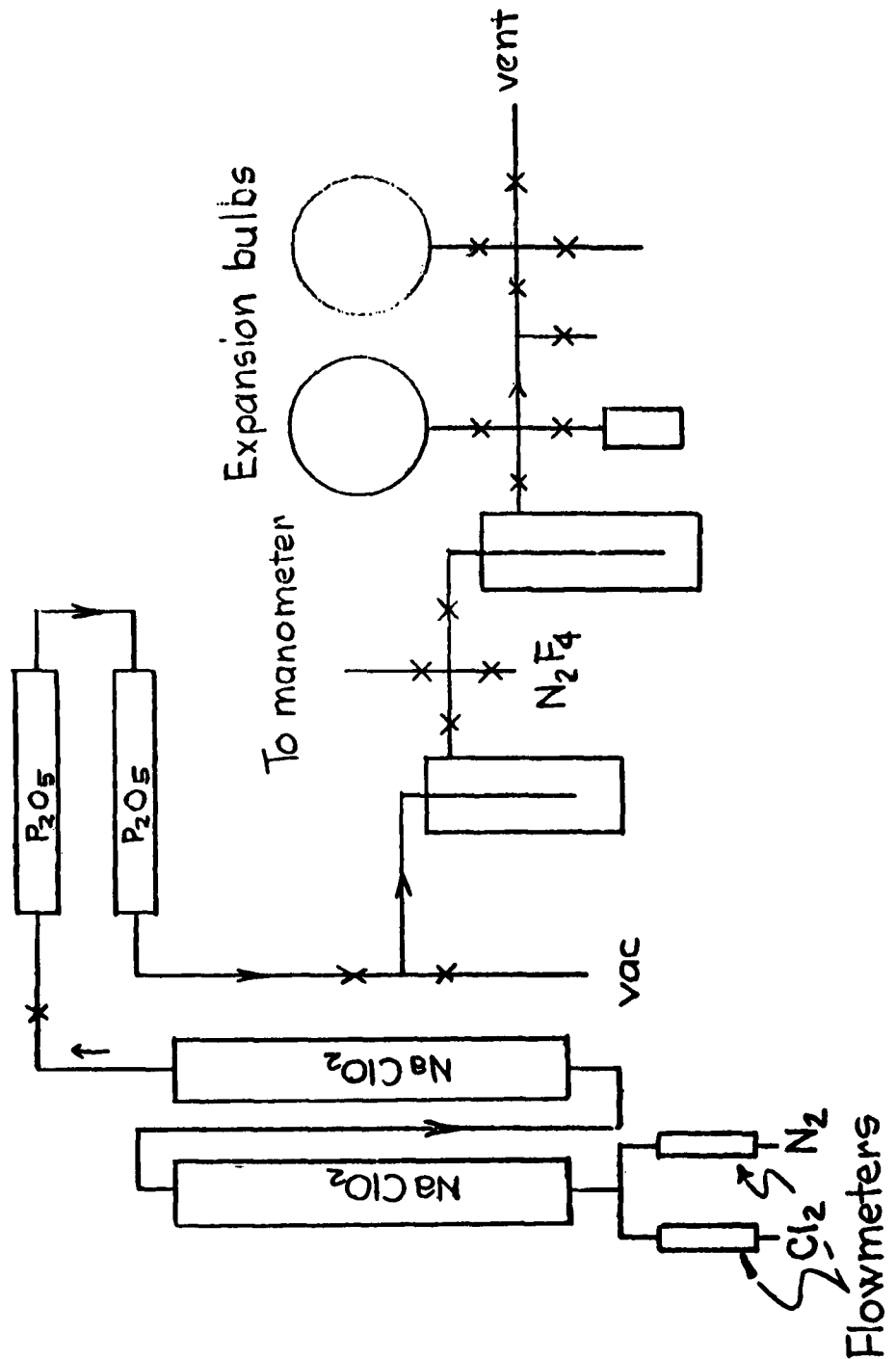
reactor was constructed of Pyrex glass.

Procedure

The Pyrex reactor was cooled to -78°C. and ClO_2 (about 1 ml.) was condensed into it. The reactor was then cooled to -196°C. and the nitrogen diluent pumped out. Tetrafluorohydrazine (1. 2 g.) was then condensed into the reactor and the reactants slowly warmed to 25°C. After standing about 1 hour at 25°C., the products were fractionated and analyzed.

Results

The results are summarized in Table 45.

It was postulated that since chlorine dioxide exists as a radical, a coupling reaction might occur between ClO_2 and NF_2 in the vapor phase to form NF_2ClO_2:

$$NF_2 \cdot + \ ClO_2 \cdot \longrightarrow NF_2ClO_2$$
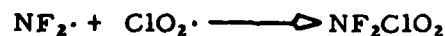
At 25°C. tetrafluorohydrazine and chlorine dioxide reacted to form a solid product which deposited on the Pyrex reactor surface and gaseous products. The gaseous products were identified as SiF_4 and nitrogen oxides. The solid product was undoubtedly $(NO)_2SiF_6$ although this solid was not isolated in amounts needed for complete characterization.

The presence of SiF_4 and nitrogen oxides in the gaseous products, coupled with the observed etching of the glass surface, indicated considerable side reaction and this approach was terminated.

Table 45

Reaction of ClO_2 + N_2F_4

Experiment	ClO_2 cc.	N_2F_4 g.	Temperature	Results
1857D-65	1	1.5	Room temp.	No indication of solid product. N_2F_4 decomposed to nitrogen oxides and silicon tetrafluoride.
1857D-68	0.5	*2.0	Room temp.	Cloudy, white deposit on walls of the reactor. Residual gases found to be nitrogen oxides and silicon tetrafluoride. Some nitrogen trifluoride and tetrafluorohydrazine also present.

* N_2F_4 contained more impurities than that in the previous materials prepared in Olin Mathieson laboratories.

Section V. Reactions with Fluorochlorine Oxides

A. Reactions with $FOClO_3$

1. Objective

In the constant search for new intermediates that could be used in the synthesis of high energy oxidizers, fluorine perchlorate was selected because it possesses two very distinct advantages

(1) The F-O bond is relatively weak (45.9 Kcal.) and can be expected to break easily.

(2) Liberation of a fluorine atom, or fluoride ion, can lead to the formation of a stable fluorine derivative or fluoride which should act as a "driving force" for certain reactions. For example:

$$NF_2 \cdots NF_2 + F \cdots OClO_3 \longrightarrow NF_2OClO_3 + NF_3$$

or

$$NF_2 \cdots H + F \cdots OClO_3 \longrightarrow NF_2OClO_3 + HF$$
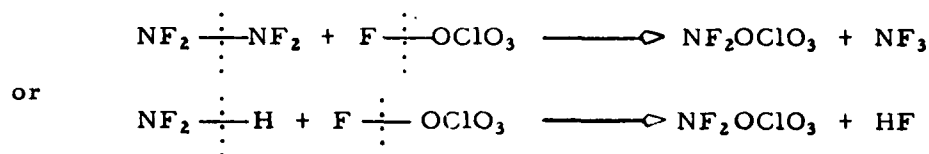
In these reactions the use of fluorine perchlorate was feasible since the reactions involved breaking of the weak O-F bond and the concomitant formation of a stable by-product NF_3 or HF. It was reasoned that if the compound NF_2ClO_4 is stable these reaction systems should produce the desired product.

A review of the literature on fluorine perchlorate indicated that the principal reasons for avoiding use of this compound by other investigators were its reported instability and difficulty in preparation. Fluorine perchlorate was first prepared by Cady and Roberback (54) by passing fluorine through a packed column containing 72 per cent perchloric acid.

Our investigation on fluorine perchlorate essentially duplicated the observations of Roberback and Cady although we found it most convenient simply to pass the fluorine through 70 per cent perchloric acid in a Pyrex glass reactor at 25° C. (See Section X for additional data and physical characterization of $FOClO_3$). Using this technique, approximately 50 grams of $FOClO_3$ was prepared. In addition, it was observed that fluorine perchlorate could be handled at ambient or room temperature without undergoing extensive decomposition.

Since fluorine perchlorate appeared to be such an attractive intermediate the use of this compound was investigated extensively.

a. $FOClO_3 + N_2F_4$

Material

N_2F_4. E. I. DuPont de Nemours and Co., Inc., Gibbstown, New Jersey. Purity 99%+.

Apparatus

Reactions in the vapor phase were conducted in the apparatus described in Figure 28. The reactor consisted of a large volume vessel (400-1000 ml.) which was interchanged with one constructed of Pyrex glass, Teflon, or Kel-F-lined steel for specific experiment. The $FOClO_3$ was stored in a 100-ml. Pyrex glass bulb and connected to a copper high vacuum line.

Reactions in the liquid phase were conducted in the apparatus described in Figure 28 except that the reactor consisted of an all Teflon vessel, described in Figure 15. The glass trap containing $FOClO_3$-CCl_4 solution was connected directly to the Teflon reactor through a line equipped with a stainless steel valve and a nitrogen inlet for pressure transfer of the $FOClO_3$-CCl_4 solution to the Teflon reactor.

Procedure

"A" Vapor Phase Reactions

In a typical experiment 0.002 g. of $FOClO_3$ was distilled into the Pyrex bulb "B", Figure 18. Reactor "A" was evacuated and 0.003 g. of N_2F_4 was diffused into the large reactor to a pressure of 0.2 atmosphere. The glass bulb "B" which contained $FOClO_3$ at 0.75 atmospheres pressure was then opened to reactor "A" and $FOClO_3$ was slowly diffused into reactor "A" where a reaction occurred. After the pressure equalized, the reactants were allowed to stand at 25°C. for approximately 30 minutes. The product was then fractionated and analyzed.

"B" Reaction in Solvents

In a typical experiment 60 ml. of carbon tetrachloride was placed in the Teflon reactor, Figure 15, and 20 ml. of carbon tetrachloride was placed in the glass bulb "B", Figure 28. The glass bulb "B" and Teflon reactor, Figure 15, were connected to a standard high vacuum copper line, Figure 28. The glass bulb "B" and Teflon reactor containing carbon tetrachloride were cooled to -78°C. and evacuated. Tetrafluorohydrazine (0.60 g.) was transferred to the Teflon reactor and fluorine perchlorate (0.50 g.) was added to the glass trap. The Teflon reactor was maintained at -78°C. while the glass bulb was warmed to 0°C. The fluorine perchlorate solution was then pressured with nitrogen into the Teflon reactor. The Teflon reactor was then warmed to 25°C. and the reactants permitted to stand for 18 hours. The product was then fractionated and analyzed.

Results

Fluorine perchlorate was expected to be a very applicable intermediate for the synthesis of NF_2ClO_4. The relatively weak F-O bond, 45.9 Kcal as compared to 110 Kcal for the O-H bond, should break readily and the following reaction was predicted with tetrafluorohydrazine

$$N_2F_4 + FOClO_3 \longrightarrow NF_2ClO_4 + NF_3$$

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Figure 28

Apparatus for N_2F_4 - $FClO_4$ Reactions
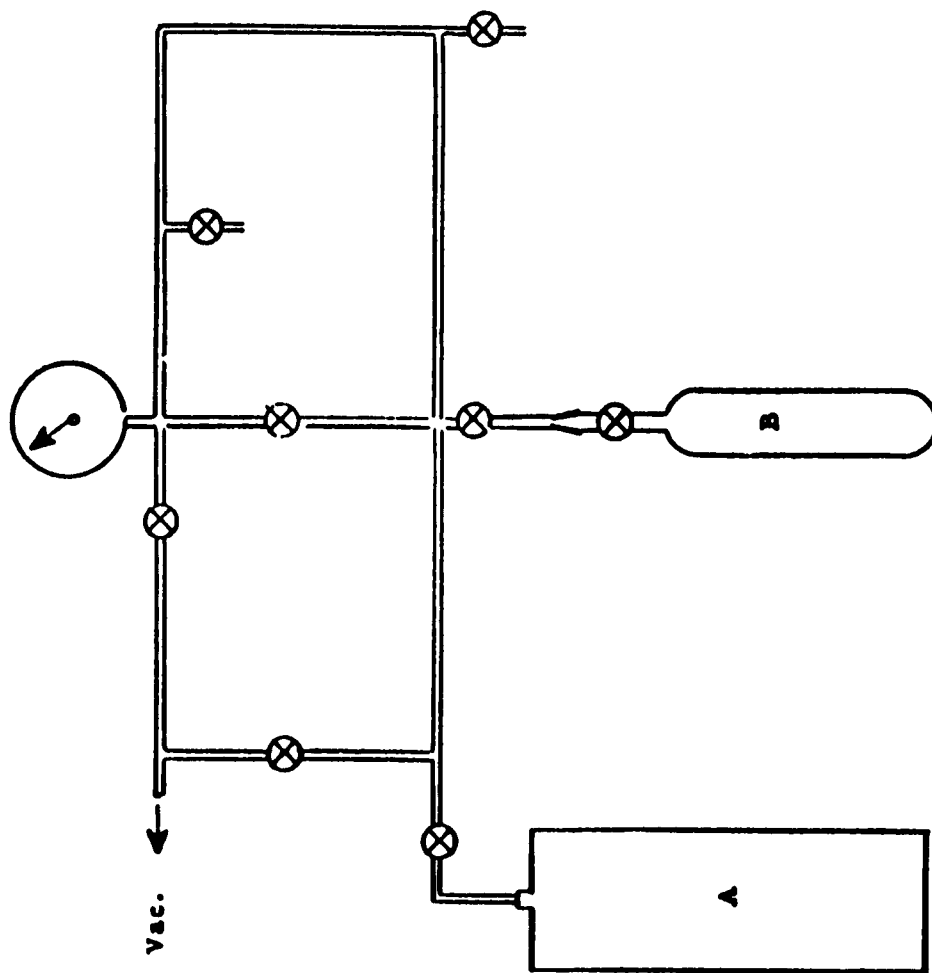
A: Reaction Vessel (Teflon, Kel-F or glass; 400-1000 ml.)
B: $FClO_4$ Transfer bulb (glass; 100 ml.)

In addition to the breaking of a weak bond, the reaction "driving force" would be augmented by the formation of a stable side product, NF_3. A major obstacle, however, was the questionable stability of the structure NF_2ClO_4. If NF_2ClO_4 is a stable configuration, it was expected that this compound would be obtained by this reaction. Considerable effort was devoted to the study of this reaction.

The results of vapor phase reactions of fluorine perchlorate with tetrafluorohydrazine are summarized in Table 46.

The first experiment in the series, 1738D-54, provided some encouraging data. A white solid product was isolated that contained 31.8 weight per cent fluorine, somewhat higher than the 25.1 weight per cent, or theoretical, for NF_2ClO_4. Volatile products from this reaction were identified as NF_3, NO_2, and NO_2F. The presence of NF_3 also heightened the belief that the desired reaction had taken place.

When the experiment was repeated (1738D-56) the reactor exploded as it reached room temperature and no product could be obtained. It was suspected that the reactor might have cracked and admitted air which caused the explosion and a Teflon reactor was employed next in experiment 1738D-58. Although there was evidence of reaction (formation of NF_3 and NO_2F) no solid product was obtained.

Efforts to repeat the original reaction to obtain additional product for characterization failed and the reactors in experiments 1738D-60, -62, -63 and -64 all exploded before the solid product could be removed.

In order to learn something of the nature of the product, the reaction system was modified in experiment 1738D-65 so that a hydrolyzing solution of aqueous sodium hydroxide could be added directly to the reactor. This was successful in obtaining a positive qualitative indication of fluorine but there was not sufficient concentration to permit a quantitative determination.

It was suspected that the explosions might be caused by a rapid attack of fluorine perchlorate on the N_2F_4. The fact that N-O-F products had been observed lent support to this contention. It also was suspected that the fluorine-containing solid product might be arising from attack on the glass, even though there appeared to be little etching of the glass reactor. This belief also was supported by the observation that N-O-F materials were formed in the Teflon reactor, with no accompanying yield of solid product. To circumvent this, in experiment 1738D-66, the $FOClO_3$ was permitted to diffuse very slowly into the N_2F_4 and a white solid did form, which appeared similar to that observed in the initial reaction.

An amount sufficient for infrared analysis was obtained and the product was identified as a mixture of $NOBF_4$ and $(NO)_2SiF_6$. This analysis confirmed the belief that silicon contamination was an integral part of the observed results.

Two additional experiments, 1738D-69 and -70, in a Kel-F coated steel reactor also led to the formation of oxidation products from the N_2F_4,

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Table 46

Vapor Phase Reactions of $FClO_4$ with N_2F_4

Experiment No.	Reactor Mat'l	Volume (ml)	Temp. (°C)	N_2F_4 (moles)	(grams)	$FClO_4$ (moles)	(grams)	Time (hrs.)	Analysis of Products Gaseous	Solid	Comments
1738D-54	glass	600	25	0.0025	0.35	0.0016	0.30	1/2	NF_3, NO_2 NO_2F	31.6 F	
1738D-56	glass	600	-78	0.005	0.8	0.0038	0.	1/6			Exploded as reactants warmed to room temp.
1738D-58	Teflon	600	25	0.0032	0.45	0.0022	0.4	1/2	N_2F_4, $FClO_4$ NF_3, NO_2F	No solid formed	
1738D-60	glass	400	25	0.0032	0.45	0.0016	0.3	1/3	NF_3, NOF NO_2F		Exploded after infrared sample was taken
1738D-62	glass	400	25	0.0029	0.4	0.0029	0.53	1/6			When nitrogen was added to bring pressure to atmospheric reaction exploded
1738D-63	glass	400	25	0.0043	0.6	0.0023	0.43				Exploded on mixing reactants
1738D-64	glass	400	25	0.0036	0.5	0.0021	0.39				Exploded on mixing reactants
1738D-65	glass	400	25	0.0032	0.45	0.0019	0.35	1/6	Not analyzed	Contained Fluorine	Solid product was hydrolyzed with NaOH solution
1738D-66	glass	400	25	0.0029	0.4	0.0015	0.28	1/3	Not analyzed	$NOBF_4$ and $(NO)_2SiF_6$	
1738D-69	Kel-F	1000	25	0.005	0.70	0.0022	0.4	1.0	NO_2, NF_3	No solid product	
1738D-70	Kel-F	1000	25	0.0054	0.75	0.0024	0.45	1.0	NO_2, NF_3 NOF	No solid product	

but no solid materials.

It thus appears that in the gas phase there is attack on the N_2F_4 by the $FOClO_3$ to form oxidized species containing N-O. Additionally, there is attack of N_2F_4, or oxidation products therefrom, on the glass, forming $NOBF_4$ and $(NO)_2SiF_6$. In experiments where a glass reactor is not used, the products containing boron and silicon do not form, but the N_2F_4 is oxidized.

It was concluded that N_2F_4 and $FOClO_3$ react in the vapor phase to yield low molecular weight decomposition products. If NF_2ClO_4 was formed the transitory existence of this product could not be detected under the conditions employed.

The presence of NF_3, NOF and nitrogen oxides in the gaseous products of the reaction of fluorine perchlorate with tetrafluorohydrazine indicated that NF_2ClO_4 may be decomposing. If this were the case, reactions in carbon tetrachloride would probably moderate the reaction and prevent decomposition. This reaction was investigated in both carbon tetrachloride and Freon-11 as solvents.

The results of experiments conducted in solvent systems are summarized in Table 47.

The first experiment was performed in a glass reactor for observation purposes, but no unusual phenomena were noted. Infrared examination of the gases at the end of the reaction indicated N_2F_4, NF_3, N_2O, NOF, NO_2F and SiF_4. No solid or liquid products separated from the final solution.

The presence of N-O and N-O-F materials indicated that some oxidation of the N_2F_4 had taken place, but the fact that some of it had remained unchanged led to continuation of the study. The appearance of silicon tetrafluoride established the fact that this material could be formed by attack on the glass reactor even in carbon tetrachloride solution. For this reason, the Teflon reactor was used in subsequent experiments.

At the completion of the second reaction a small fluorine containing globule, about 2 mm. in diameter, was noted at the bottom of the reactor. Several additional experiments were then performed to obtain more product for testing and characterization.

The viscous liquid liberated iodine from potassium iodide and reacted with anhydrous hydrazine, both of which indicated oxidizing properties. Identification of NF_3 in the gaseous products at the completion of some of the experiments increased speculation that the desired reaction might have occurred. Elemental analyses, however, especially for fluorine, were quite variable and values ranged from a low of zero to 62.9%.

The liquid was very reactive, etching glass and attacking many materials of construction. It was difficult to manipulate and was converted to a paste when attempts were made to completely remove all of the carbon

Table 47

Liquid Phase Reactions of FClO$_4$ with N$_2$F$_4$

Expt. No.	Weight FClO$_4$ (g)	Weight N$_2$F$_4$ (g)	CCl$_4$ N$_2$F$_4$/FClO$_4$ Solvent ratio (ml.)	Time (hrs.)	Temp. °C	REMARKS
1583-70 (a)	0.24	3.30	10/10	18	-8 to 25	Infrared analysis of gaseous products: NF$_3$, N$_2$O, NOF, NO$_2$F, SiF$_4$
-74	0.32	0.50	50/0	1	-78 to 25	Infrared analysis of gaseous products: NF$_3$, NOF, FClO$_4$ Infrared analysis of CCl$_4$ Sol b: NO$_2$, NOCl: small globule noted in bottom of reactor (b)
-80	0.10	0.20	10/10	2	-78 to 50	Infrared analysis of CCl$_4$ Sol b: HClO, NOCl, NO$_2$ Infrared analysis of globule: reacted with NaCl and BaF$_2$ cell windows--also those 'protected' with polyethylene film
-82	0.30	0.40	20/15	18	0 to 25	Infrared analysis of globule: reacted with BaF$_2$ cell windows, only ClO$_4^-$ absorption.
-89	0.28	0.40	15/15	18	-78 to 25	Globules combined: Infrared analysis: reacted with BaF$_2$ cell coated with fluorolube; elemental analysis: 62.9%F, 3.5%Cl
-93	0.30	0.40	15/15	2	-78 to 25	
-94	0.42	0.55	15/25	1	-78 to 25	
-96	0.44	0.50	50/25	2		Infrared analysis of globule: KBr pellet, ClO$_4^-$, NO$^+$
-97	0.42	0.55	50/20	2		Elemental analysis: 0%F, 25.5%Cl, 6.3%N
-98	0.35	0.50	50/25	44		Infrared analysis of globule: Attacked Irtran cell
2337D-7	0.50	0.60	50/15	18		Elemental analysis: 46.3%F, 10.83%Cl
-9	0.52	0.60	50/20	18		Infrared analysis of globule: Attacked AgCl cell
-10	0.45	0.50	55/20	18		Product formed NO$_2$, NOCl, NaHF$_2$ when placed in a NaCl infrared cell
-11	0.45	0.55	50/20 (c)	18	-78 to 25	Product same as previous experiments. Elemental analysis 54.7%F. Aliquot of product taken to dryness-X-ray showed NOClO$_4$
-18	2.00	2.50	250/40	15	-78 to 25	Paper chromatographic analysis of globule: F$^-$, NO$_2^-$, NO$_3^-$, ClO$_4^-$. Paper chromatographic analysis of solid formed after globule removed and open reactor exposed to atmosphere: NOClO$_4$
-25	1.50	0.80	130/20 (d)	4	-78 to 25	Excess FClO$_4$, no product formed.
-27	0.60	1.10	130/20	3	-78 to 25	g. Product/g. reactants = 6.67% yield
-28	0.75	1.10	130/25	18	-78 to 25	g. Product/g. reactants = 3.70%
-29	1.05	1.50	130/25	18	-78 to 25	g. Product/g. reactants = 1.60%. Infrared analysis showed HF and NO$^+$ C$_2$F$_2$ cell employed
-30	1.00	1.20	130/20 (e)	3	-78 to 25	g. Product/g. reactants = 4.20%

(a) glass reactor
(b) similar product noted in all subsequent experiments, except 2337D-25
(c) CCl$_4$ distilled from KMnO$_4$ and P$_2$O$_5$
(d) Freon-11 substituted for CCl$_4$
(e) CCl$_4$ contained 0.05% added water (by weight)

tetrachloride. Infrared examination was attempted, but the liquid attacked the sodium chloride, Irtan, silver chloride, barium fluoride and polyethylene-coated cell windows. With the use of KBr pellet and calcium fluoride cell windows, however, it was possible to establish the presence of HF and the ions NO^+ and ClO_4^-.

One sample of the product was placed in an infrared gas cell and warmed to observe the gaseous decomposition products, if any. These proved to be NO_2, $NOCl$ and HF, with the residue being a paste. The presence of $NOClO_4$ in the residue was established by X-ray.

Paper chromatographic analysis indicated perchlorate, nitrite or nitrate, and fluoride ions. This information confirmed only the presence of perchlorate since the other ions all could conceivably have arisen from hydrolyses of N-F bonds.

These results have led to the tentative conclusion that the product to date was a mixture of $NOClO_4$ and possibly some HF complex. Such complexes with NOF and NO_2F are known which may contain as many as five HF molecules of complex. This could account for the varying fluorine analyses and the observed physical characteristics since some of these complexes boil in the range 60-92°C.

One experiment was conducted to evaluate the effects of greater than stoichiometric amounts of $FOClO_3$ but no product was obtained. The excess $FOClO_3$ may have caused decomposition of the product.

Reaction conditions had little affect on the product. Changes in temperature and reaction produced no corresponding changes in the product. An increase in the amount of starting materials did not result in an increased quantity of product. The use of Freon-11, instead of carbon tetrachloride, as solvent also did not alter the product. In addition, no change could be detected when the carbon tetrachloride was first distilled over both potassium permanganate and phosphorous pentoxide.

Trace amounts of water are suspected of causing the observed phenomenon but this has not been proved. Both the $FOClO_3$ and the N_2F_4 are susceptible to decomposition by water and a possible reaction sequence is

$$FOClO_3 + H_2O \longrightarrow HF + HClO_4 + 1/2\, O_2$$

$$N_2F_4 + O_2 \longrightarrow NOF + NF_3$$

$$NOF + HClO_4 \longrightarrow HF + NOClO_4$$

$$xHF + NOF \longrightarrow NOF \cdot xHF$$
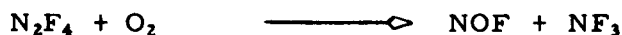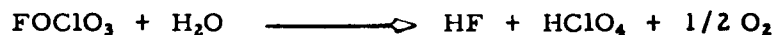
Some of the observed results, however, are not consistent with such a scheme. It is difficult, for example, to explain the absence of product when an excess of $FOClO_3$ was used.

A search was initiated for a polar solvent for fluorine perchlorate in which ionic reactions would be formed. Although preliminary evidence indicated that SO_2 was satisfactory, later studies revealed that fluorine perchlorate reacts with sulfur dioxide even at -78°C. over a period of several hours to form SO_2F_2 and SF_6.

The reaction of tetrafluorohydrazine with fluorine perchlorate in carbon tetrachloride and Freon-11, as well as reactions in the vapor phase, did not yield the desired product NF_2ClO_4 under the conditions used.

b. $FOClO_3 + NF_2H$

Material

NF_2H. Prepared by the reaction of thiophenol with tetrafluoro-hydrazine as described in Section X.

70% $HClO_4$. Mallinkrodt Chemical Co., Reagent Grade.

SO_2. Allied Chemical and Dye Corp., General Chemical Division.

Apparatus

A general purpose copper tubing high vacuum line is described in Figure 28. Two reactor designs were used. Reactor "A" consisted of a one-liter Pyrex vessel and reactor "B" consisted of a copper tubing coil. Reactions in SO_2 were conducted in a Kel-F reactor equipped with stainless steel inlets. This reactor was connected to the high vacuum line described in Figure 28.

Procedure

In a typical experiment difluoramine and fluorine perchlorate were placed in separate metal cylinders and the metal cylinders were connected to a copper high vacuum line. A measured quantity of NF_2H was admitted to the reactor and a measured amount of $FOClO_3$ was transferred from the steel cylinder to a small glass trap attached to the transfer line. The $FOClO_3$ was allowed to diffuse slowly into the reactor containing the NF_2H. In some experiments the reactants were diluted with nitrogen to moderate the reaction. After diffusion of the gases was complete (generally 15 minutes) the products were fractionated and analyzed.

In a typical experiment with SO_2 as a solvent, sulfur dioxide (dried over P_2O_5) was condensed into the Kel-F reactor and a measured quantity of NF_2H was added to the SO_2. The mixture was shaken to insure complete solution. Excess or undissolved gases were pumped out. A weighted amount of fluorine perchlorate was then condensed onto the solution and the reactants were allowed to stand, generally at -50°C., for 18-60 hours. The products were then fractionated and analyzed.

When 70% perchloric acid was used as a solvent, the aqueous

perchloric acid was first saturated with difluoramine and then fluorine perchlorate, diluted with nitrogen, was bubbled through the solution or simply passed over the liquid surface.

Results

The reaction of difluoramine with fluorine perchlorate was investigated since the following reaction appeared to be a reasonable approach to the synthesis of NF_2ClO_4

$$FOClO_3 + NF_2H \longrightarrow NF_2ClO_4 + HF$$

In this case the rupture of a weak F-O bond (45.9 Kcal) and the formation of a stable side product, HF, was expected to favor the formation of NF_2ClO_4. A calculation of the heat of reaction, using estimated heats of formation for $FOClO_3$ and NF_2ClO_4 of +31 and +26 Kcal/mole, respectively, results in a value of -51.2 Kcal/mole, thus, indicating that the desired reaction could occur.

The reaction of difluoramine with fluorine perchlorate was conducted in the vapor phase and in solvent systems such as sulfur dioxide and 70% aqueous perchloric acid. The results of reactions in the vapor phase are summarized in Table 48.

In the vapor phase, the reaction of NF_2H with $FOClO_3$ was vigorous, generally resulting in an explosion. Therefore, various modifications of apparatus and procedure were tried to provide better reaction control.

In experiment 1583-59, Table 48, the first of this series, a glass reactor was used so that pertinent observations on the behavior of the two reagents could be made. It was expected that the reaction might be vigorous and for that reason a temperature of -78°C. was selected. The mixture detonated, however, and the products were lost. The use of 10 ml. of carbon tetrachloride as solvent and moderator for the reaction was successful in preventing detonation at -78°C. but when the temperature reached +25°C., the mixture again detonated.

Nitrogen gas as a diluent and a glass-free system also were employed but these, too, did not prevent detonation.

Since the reaction mixture had appeared to be stable below 25°C. in the presence of an inert moderator, a metal spiral which could be cooled was designed as the reactor. This change and a corresponding reduction in quantities of reagents were successful in bringing the reaction under control and a sample of the product gases was obtained for analysis.

The gas was a mixture of NOF, NO_2F and NO_2 along with some of the unreacted reagents. It thus appears that there is oxidation of the HNF_2 by the $FOClO_3$, forming N-O and N-O-F products. The absence of HF in the products does not necessarily mean that none of the desired reaction took place, because HF is difficult to detect in low concentration in the infrared spectrum. There was no evidence, however, for absorption bands corresponding to NF_2ClO_4.

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Table 48

Vapor Phase Reactions of $FClO_4$ with HNF_2

Expt. No.	$FClO_4$ (g.)	HNF_2 (g.)	Time (min.)	Temp. (°C)	Nitrogen Dilution (by vol)	Reactor	Remarks
1583-59	0.07	0.15		-78		glass trap	Mixture detonated at -78°
-60	0.07	0.08		-78		glass trap	10 ml CCl_4 added—mixture detonated while warming to 25°C
-61	0.10	0.10		25	70	metal line	Mixture detonated
-63	0.10	0.10		25	70	metal line	Mixture detonated
-64	0.04	0.02	15	-8 to 25	65	metal spiral	Infrared of gaseous products: NOF, NO_2F, $FClO_4$, NO_2, trace HNF_2
-65	0.10	0.03		0	50	metal spiral	Mixture detonated; Infrared of decomposition gases: NF_3, NO_2
-66	0.07	0.05		-8	65	metal spiral	Mixture detonated

It is conceivable that the material formed and the NF_2 and ClO_4 bands of this product were masked by the absorptions of the NF_2H and $FOClO_3$, but there is no real justification for this contention.

Two additional experiments in the series, 1583-65 and -66, were performed but vigorous decompositions were noted. The presence of NF_3 and NO_2 was detected in the decomposition products from the first of these two experiments but no corresponding analyses could be made in the latter experiment.

Reactions of difluoramine and fluorine perchlorate in the vapor phase did not provide any firm data on the feasibility of this approach to the synthesis of NF_2ClO_4 due to the extreme reactivity of these reactants. Better reaction control was obviously needed and the use of inert solvents was the most logical choice. If heterolytic bond cleavage of $FOClO_3$ occurs in a polar solvent, several new products could result. The various possibilities are listed below·

$$(1) \quad \overset{\delta+}{H} - \overset{\delta-}{NF_2} + \overset{\delta-}{F} - \overset{\delta+}{OClO_3} \longrightarrow NF_2ClO_4 + HF$$

$$(2) \quad \overset{\delta+}{H} - \overset{\delta-}{NF_2} + \overset{\delta+}{FO} - \overset{\delta-}{ClO_3} \longrightarrow NF_2OF + HClO_3$$

$$(3) \quad \overset{\delta+}{H} - \overset{\delta-}{NF_2} + \overset{\delta-}{FO} - \overset{\delta+}{ClO_3} \longrightarrow NF_2ClO_3 + HOF$$

$$(4) \quad \overset{\delta+}{H} - \overset{\delta-}{NF_2} + \overset{\delta+}{F} - \overset{\delta-}{OClO_3} \longrightarrow NF_3 + HClO_4$$
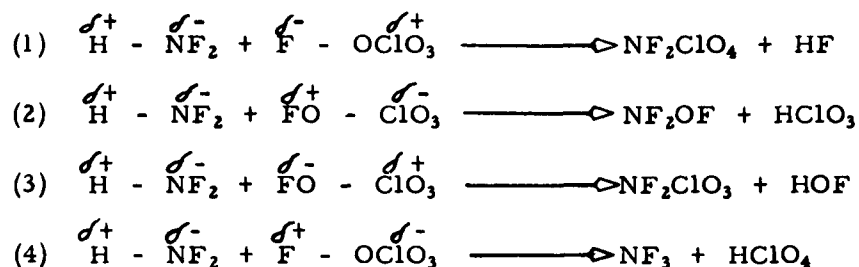
The reactions of difluoramine with fluorine perchlorate in sulfur dioxide are summarized in Table 49.

The gaseous products of the reaction were mainly N_2F_4 and NF_3. In one case NF_2Cl was also identified as being present. Removal of the SO_2 solvent left a colorless liquid which had a fluorine nuclear magnetic resonance spectra of 37.5 ppm to the low field side of CCl_3F. Furthermore, all the fluorine atoms present were identical. A proton NMR spectrum showed the presence of hydrogen. Rohm and Haas (45) has prepared the compound NF_2SO_3H from the reaction of NF_2H with SO_3 and reported fluorine and proton NMR spectra which were almost identical to that found for our liquid product. Several attempts to purify and characterize all of the products in the liquid were unsuccessful but the presence of only one type of fluorine in the mixture eliminates the possibility that NF materials other than NF_2SO_3H were present.

The NF_2SO_3H probably arises from oxidation of some of the SO_2 to SO_3, which then reacts with HNF_2. The formation of N_2F_4 and NF_3 suggests that homolytic bond cleavage of the $FOClO_3$ is occurring. Several suggested reactions to explain the results are given on the following page.

Table 49

Reaction of FOClO₃ with NF₂H in Sulfur Dioxide

Exp. No.	Reactants NF₂H wt. gms	moles	FOClO₃ wt.	moles	Solvent ml.	Reaction Temp. °C	Reaction Time hrs.	Gaseous Reaction product	Liquid Products	Comments
1738D-90	0.20	0.0038	0.42	0.0036	40	-78 to -50	60	NF₃	Positive KI	
1738D-93	0.41	0.0077	0.63	0.0053	40	-78 to -50	20	NF₃,N₂F₄ 0.185 g. at -78°C	NMR analysis: covalent fluorine-only one kind;37.7 ppm on low field side of CCl₃F; proton present	No noncondensibles
1738D-96	0.32	0.006	0.61	0.0052	40	-78 to 0°C	60	NF₃,N₂F₄ 0.100 g.at -78°C	2.5%N; 12.3%S; 16.3%F	No noncondensibles
1738D-99	0.42		0.79		50	-78 to -50	18	NF₃,N₂F₄	0.42%Cl	Chlorine determined on material remaining after distillation at 40°C and 0.1 mm
1738D-102	0.30		0.62		45	-78 to -50	18	NF₃	0.31%Cl	
367405	0.77		0.43		40	-78 -50	18 3	NF₃,N₂F₆, NF₂Cl	0.28 g; 1.9%N, 10.2%Cl, 18.4%F 28.4%S	

$$NF_2H + FOClO_3 \longrightarrow NF_2 + HF + ClO_4$$

$$2NF_2 \cdot \longrightarrow N_2F_4$$

$$ClO_4 \cdot + SO_2 \longrightarrow SO_3 + \text{chlorine oxides}$$

$$NF_2H + SO_3 \longrightarrow NF_2SO_3H$$

$$NF_2 \cdot + FOClO_3 \longrightarrow NF_3 + ClO_4 \cdot$$

$$NF_2 \cdot + \text{chlorine oxides} \longrightarrow NF_2Cl$$
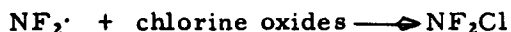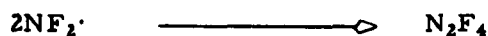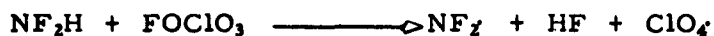
Satisfactory material balances for the chlorine containing products were not obtained. Although NF_2Cl was observed as one of the products, this was not a general occurrence and it was found in only one case. Elemental oxygen and nitrogen are not liberated since all the products are condensible at -196°C. It appears that chlorine oxides are formed which then react with sulfur dioxide to form SO_3 and other unidentified sulfur-chlorine-oxygen products.

The interaction of sulfur dioxide solvent was discouraging, consequently, the reaction of difluoramine with fluorine perchlorate was investigated in 70 per cent aqueous perchloric acid as solvent. The results of these experiments are summarized in Table 50.

When fluorine perchlorate was added to a solution of difluoramine in aqueous perchloric acid, there was no apparent reaction in the liquid layer, but a detonation occurred in the gas phase above the solution after only a small quantity of $FOClO_3$ had been added (Exp. 1887-103 Table 50).

Apparently rapid reaction occurred when a sufficient quantity of $FOClO_3$ had bubbled through the solution and entered the gas phase. In experiment 1887-105, conducted in a similar manner, a detonation was not observed but the products including N_2F_4, N_2O, NO_2 and NF_3 were identical. Apparently fluorination and oxidation of the NF_2H results. When fluorine perchlorate is added directly to the gas phase above the perchloric acid-difluoramine solution (evacuated just prior to addition to remove NF_2H in the gas phase) similar results are obtained.

Apparently, the 70 per cent perchloric acid has served as an inert diluent and any reaction between NF_2H and $FOClO_3$ occurs only in the gas phase. Since the fluorine perchlorate is fairly insoluble in the perchloric acid and the solvent did not increase the rate of reaction between the two components, the vapor above the solution contains most of the $FOClO_3$. The low solubility of $FOClO_3$ in perchloric acid was somewhat surprising. Fluorine perchlorate is prepared by bubbling fluorine through 70 per cent perchloric acid and the fluorine perchlorate is not released immediately suggesting that the solution is dissolving the fluorine perchlorate as it forms. In the absence of the solvent the products which result are also N-O materials (Exp. 1691-98). The major reaction products include N_2F_4, NF_3, NO_2F, NOF and NO_2.

The reaction appears to take place by hydrogen abstraction followed

Table 50

Reaction of NF₂H with FClO₃ in 70% HClO₄

Expt. No.	NF₂H g	FClO₄ g	Temp. °C	Reactor	HClO₄ 70% ml	Results and remarks
1691-94	0.014 g. in sol. 0.030 g. overhead	0.015 g. cat.	0°C	Teflon-Teflon coated glass top 4/ml	2 ml.	Vapor-vapor reaction - overhead NF₂H removed by rapid vacuum distillation before introduction of FClO₄ - N₂ 1:5, overhead N₂O, NO₂, SiF₄ trace FClO₄
1691-96	0.044 g. in sol. 0.055 g. overhead	0.045 g. calc.	0°C	"	10 ml	Vapor-vapor contact first - overhead NF₂H removed by rapid vacuum distillation before introduction of FClO₄ - N₂ 1:5 N₂O₃, N₂F₄, NO₂, NF₂H (FClO₃ trace) overhead after reaction
1691-98	0.010 calc.	0.020 g. calc.	0°C	"	no solvent	Small erratic pressure surges noted on mixing M.S. NO₂F, (NOF), FClO₃ trace
1887-103	0.31 g.	** approx. 80 mg	0°C	Stainless steel-Kel-F	10 ml	**Reaction and addition stopped after detonation occurred. N₂F₄, NO₂, N₂O, NF₃
1887-105	0.24	0.105	0°C	Stainless steel-Kel-F	10 ml	No detonation noted overhead N₂F₄, N₂O, NF₃, NO₂, trace FClO₃ / Absorption in I.R. of perchloric acid (70%) solution too strong. No liquid analysis attempted.

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by oxidation, fluorination and coupling. The formation of trace amounts of perchloryl fluoride might suggest OF radical formation. However, $FClO_3$ is also a minor constituent of the thermal decomposition of $FOClO_3$. A reaction mechanism which would explain the products found is as follows:

$$NF_2H + FOClO_3 \longrightarrow NF_2\cdot + HF + ClO_4\cdot$$

$$NF_2\cdot + NF_2\cdot \longrightarrow N_2F_4$$

$$NF_2\cdot + FOClO_3 \longrightarrow NF_3 + ClO_4\cdot$$

$$NF_2\cdot + ClO_4\cdot \longrightarrow NOF, NO_2F, NO_2$$
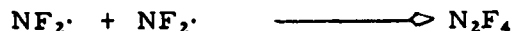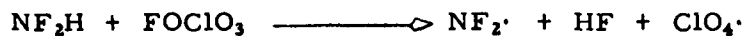
The limited data obtained from these investigations was frequently difficult to interpret and consequently firm conclusions regarding the reaction cause and product composition could not be made. However, it can be stated that the reaction of fluorine perchlorate with difluorimine is rapid and some means of reaction control is necessary if the desired product, NF_2ClO_4, is to be isolated. A suitable solvent for this reaction was not found. This reaction merits further investigation in inert solvent systems.

There was no real evidence for the formation of NF_2ClO_4 in this study but it was not shown conclusively that NF_2ClO_4 did not form and immediately decomposed to the products found.

c. $FOClO_3 + NF_3$

Material

NF_3. Peninsular Chemical Research, Inc.

Apparatus

Reactions in the vapor phase were conducted in a 200-ml. stainless steel cylinder which was attached to a general purpose metal high vacuum line.

Electric discharge reactions of fluorine perchlorate and nitrogen trifluoride were conducted in the apparatus described in Figure 29.

The gases were subjected to an electrical discharge of 5-15 KV in an evacuated system. The reactor was a U-tube made of quartz or Pyrex and the electrodes were Monel metal rods 2 mm. in diameter. The electrode gap varied in the experiments between 3 and 12 cm. The vacuum line was a metallic type (copper tubing, brass sleeves and joints, nickel valves, Monel traps) except for the 500-ml. storage bulb made of Pyrex glass. The line was flamed and evacuated before each experiment. The newly assembled line was fluorinated for 24 hours with chlorine trifluoride before use.

Lubricants were avoided wherever possible and Kel-F fluorocarbon grease was employed when necessary. The Pyrex storage bulb served as a reservoir of reactant gases and could be filled and evacuated through a 3-way vacuum stopcock. The pressure was estimated with two metal vacuum gauges,

Figure 29

Electrical Discharge Apparatus
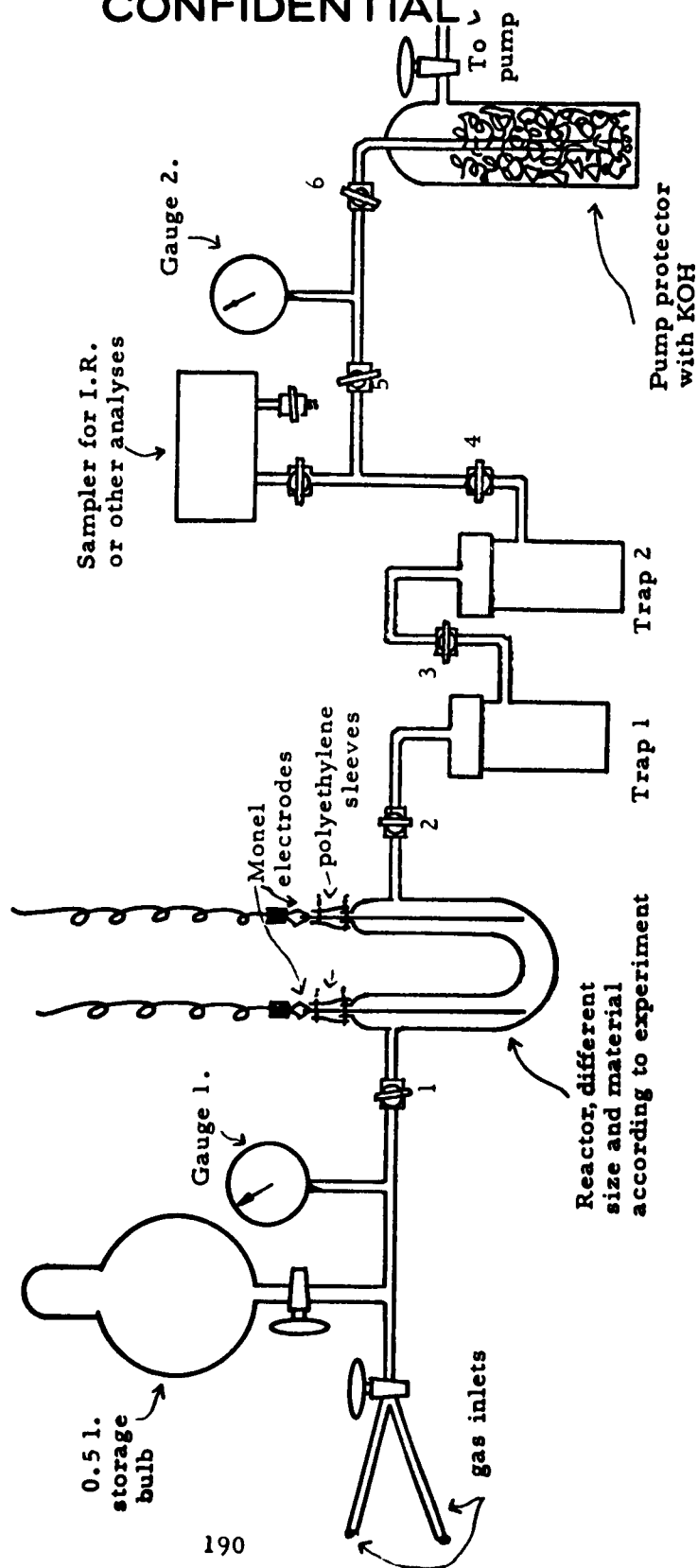
which were checked with a McLeod gauge and found to be reliable down to 0.25" vacuum.

Procedure

"A"-Vapor Phase Reactions

Fluorine perchlorate is condensed into a stainless steel cylinder followed by the addition of nitrogen trifluoride. The gas mixture is warmed to room temperature and the pressure measured. The gases are then heated to 230°C. over a period of one hour. Periodic pressure measurements are made during the heating cycle. The product is then fractionated and analyzed.

"B"-Electric Discharge Reactions

The storage bulb, Figure 29, is filled with the reactant mixture to give a total pressure of one atmosphere; the remaining portion of the line is under vacuum. A coolant is placed around the reactor and a bath of liquid nitrogen around trap 1. The discharge is started producing a continuous, broad, bluish-pink band between the electrodes. Valve 1 is closed and the stopcock for the storage bulb is opened. Needle valve 1 is now slowly opened which permits the gas mixture to flow into the reactor, during which time valve 6 is closed. The discharge assumes a deep purple color. Needle valve 1 maintains the gas flow at a pressure drop of about 1/2" to 1" per minute, as measured on gauge 1. Needle valve 6 is then opened so that the pressure reading on gauge 2 is about 1/2" to 1 3/4", a pressure sufficient to maintain an even flow and optimum pressure for a broad discharge. At the completion of the experiment valves 1, 2, 3, 4 and 6 are closed and the discharge is turned off. A brown solid is generally visible in the reactor. The products are then permitted to warm and are recondensed at -196°C. This decomposes any of the higher fluorine oxides. Bulb to bulb fraction distillation then is conducted and the various gas fractions are analyzed by infrared spectrometry.

Results

The vapor phase reactions of fluorine perchlorate with nitrogen trifluoride are summarized in Table 51.

The compound $NF_3 \longrightarrow O$, reported by both Allied Chemical Co[46] and Rocketdyne[106] can be synthesized from NF_3 and oxygen in a discharge tube. This is the first example of coordination of the unpaired electrons on nitrogen in NF_3. Previous attempts to show the availability of these unpaired electrons were uniformly unsuccessful. The formation and stability of this compound suggest that NF_3, when properly activated, can and will enter into reactions involving its unpaired valence electrons in the presence of powerful electrophilic reagents. It was of interest to determine whether fluorine perchlorate will function as such an electrophilic reagent

$$F_3N: + FOClO_3 \longrightarrow (F_3N:F)^+ (ClO_4)^-$$

The initial reactions were conducted in the gas phase using only

Table 51

Gas Phase Reaction of $FOClO_3$ with NF_3
(Heated to 230°C)

	Run 1		Run 2	
	Conc., Start (mmoles)	Conc. Completion (mmoles)	Concs. Start (mmoles)	Conc. Completion (mmoles)
$FOClO_3$	0.770		1.04	0.05
NF_3	0.490		1.05	1.05
Impurities	0.0		0.09	
Dec. Products				3.03
TOTAL	1.26		2.18	
Recovered, Total		2.11		4.13
Ratio Recovered / Start		1.68		1.9

thermal   activation although it was considered doubtful that the reaction suggested above would occur in the absence of a polar mechanism. Free radical attack by a fluorine or perchlorate radical on the nitrogen of NF_3 is not feasible since the attacking radical must have an empty valence orbital to add to a neutral nitrogen trifluoride. However, abstraction reactions did offer promise for the formation of new oxidizers, as in the following example.

$$FClO_4 \longrightarrow F\cdot + ClO_4\cdot$$

$$NF_3 + F\cdot \longrightarrow \cdot NF_2 + F_2$$

$$NF_2 + ClO_4\cdot \longrightarrow NF_2ClO_4$$
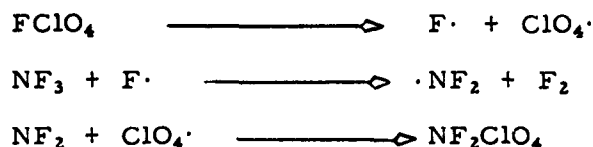
When fluorine perchlorate and nitrogen trifluoride were heated in a steel cylinder no significant pressure change occurred other than that due to expansion of the gases until the temperature had increased above 150°C. At this temperature and above, the pressure increased steadily. The volume of the system had previously been calibrated so that the total moles of gas present could be determined. Gas samples were removed from the reactor and placed in another bulb of known volume and weight and from the pressure-volume-temperature relationship, the average molecular weight was calculated. The gas was also analyzed by infrared. Molecular extinction coefficients were determined and used to obtain quantitative data on the concentration of fluorine perchorate and nitrogen trifluoride. The extinction coefficient numerical values are listed in Figure 30.

Molecular weight determination and infrared analyses of various fractions indicated that only low molecular weight products were formed. No evidence for the formation of a product having a molecular weight greater than that of $FOClO_3$ was obtained. The ratio of starting and final pressure indicated that only partial decomposition of $FOClO_3$ had occurred. In run 2., Table 51, it was definitely shown by quantitative infrared analysis that NF_3 did not participate in any reaction with $FOClO_3$ or its decomposition products. The results indicate that thermal decomposition of $FOClO_3$ results with the formation of diatomic gases.

$$FOClO_3 + NF_3 \longrightarrow NF_3 + 1/2F_2 + 1/2Cl_2 + 2O_2$$
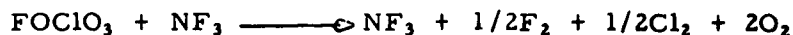
The ratio of starting and final pressure, if the above situation occurs, would be 3:1 (correcting for the pressure of NF_3 and impurities). Experimentally, the ratio was 2.9:1.

It was concluded that in the vapor phase NF_3 does not react with fluorine perchlorate. Above 150°C. fluorine perchlorate is thermally decomposed and the nitrogen trifluoride can be recovered.

Electric discharge reactions of fluorine perchlorate and nitrogen trifluoride are summarized in Table 52.

The synthesis of NF_3O by electrical discharge indicates that, with

Infrared Molecular Extinction Coefficients
For $FClO_4$, NF_3, and ClF_3

Molecular extinction coefficients of some oxidizer intermediates were determined from infrared spectra,

Molecular extinction coefficient $E = \dfrac{M}{C\,d}\ \log \dfrac{I_0}{I}$

where C = concentration in grams/liter

M = molecular weight

d = cell thickness

$\dfrac{I_0}{I}$ = intensity ratio of incoming and transmitted light

1. **Fluorine Perchlorate ($FOClO_3$)**

Wavelength (microns)	E	Remarks
7.7	720-750	Very strong band
9.55	130-190	
11.3	22-35	

2. **Chlorine Trifluoride (ClF_3)**

14.5	22.37	Weak band at end of range offering only limited possibilities for quantitative analysis.

3. **Nitrogen Trifluoride (NF_3)**

4.6	0.9
5.2	4.9
5.5	2.8
6.5	0.8
8.8	1.6
9.7	57.3
11.0	339.0

Table 52

Electrical Discharge Reactions

Exp. No.	Gas Mixt. m.Mole	ratio	tube	electrode	E.D. gap	KV	Min.	T-°C	Pmm	I.R.BaF₂ cell, 50mm Hg gas analysis %	Solid
15	7 NF₃ 3.5 FClO₄	2:1	Pyrex	Monel	3	5	25	119	10	NF₃ 42.6 NO₂ 29.95 NOCl 14.0 SiF₄ 13.45	-
17	13.7 NF₃ 1.8 FClO₄	8:1	"	"	3	5	26	196	10	FClO₄ 36.7 NF₃ about 66	-
18	20.6 NF₃ 10.3 O₂	2:1	"	"	3	15	15	196	6-10	F₃NO 3.85 NF₃ 40.0 N₂O 54.15	-
19	10 NF₃ 10 N₂F₄	1:1	"	"	3	5	22	196	6-10	NF₃, N₂F₄ trace of NOF, N₂O	-
20	8.7 NF₃ 8.7 N₂F₄	1:1	"	"	3	5	60	196	10	NF₃ N₂F₄ NOF N₂O	White solid at room temp. decomp. (NO₂)₂SiF₆
21	10 N₂F₂ 10 FClO₄	1:1	SiO₂	Fe	5	5	35	196	10-12	N₂F₂ N₂F₄ NF₃ NOCl, N₂O	-

proper activation, the unpaired electrons in NF_3 can be made available for coordination. Since the reaction can be considered as developing by reaction of an activated NF_3 with the very strong acid, oxygen atom,

$$NF_3^* + \cdot \ddot{O} \cdot \longrightarrow NF_3 \longrightarrow O$$

the use of even stronger acids may also lead to bond formation. The fluorine cation, F^+, is a much stronger acid than the oxygen atom, and could serve in a similar capacity to O in the NF_3 reaction.

A series of electric discharge reactions was conducted with mixtures of nitrogen trifluoride and fluorine perchlorate, with the perchlorate anion serving as a stabilizing influence for any cation that might form.

$$NF_3 + FOClO_3 \xrightarrow{e} NF_4^+ ClO_4^-$$

When nitrogen trifluoride alone was activated in the electric discharge apparatus, partial decomposition of NF_3 occurred with the formation of SiF_4 and nitrogen.

In the initial experiments, NF_3 and $FOClO_3$ were activated by electric discharge while the reactor temperature was maintained at $-119°C$. At this temperature complete disappearance of the $FOClO_3$ resulted with the formation of decomposition products (experiment 15, Table 52). The products were mainly SiF_4, NO_2 and NOCl. When the reactor or discharge tube was cooled to $-196°C$., essentially complete recovery of the reactants was obtained, Experiment 17.

In this preliminary investigation of electric discharge activation of NF_3 and $FOClO_3$, there was no evidence that the desired product NF_4ClO_4 was formed. However, the interaction of the glass system, as evidenced by the presence of SiF_4 in the products, again complicated the system. If reliable data were to be obtained, it was believed that a special discharge tube of Teflon or some other inert material would be required. On this basis, no further discharge experiments were conducted.

d. $FOClO_3 + N_2F_2$

Material

    N_2F_2. Air Products Company

    SO_2. The Matheson Company, Inc.

Apparatus

    "A" - Reactions in Sulfur Dioxide

    The reactor consisted of a 200-ml. stainless steel cylinder which was attached to a general purpose copper tubing high vacuum line described in Figure 28.

"B" - Electric Discharge Reactions

The electric discharge apparatus is described in Figure 29.

Procedure

"A" - Reactions in Sulfur Dioxide

To a cooled metal reactor (-78°C.) containing 0.032 g. of FOClO$_3$ dissolved in 6 g. of SO$_2$, 0.17 g. of N$_2$F$_2$ is added. The cylinder is then closed and the reactants allowed to stand at -78°C. for 16 hours. The product is then fractionated and analyzed.

"B" - Electric Discharge Reaction

The storage bulb, Figure 19, is filled with 10 millimoles of N$_2$F$_2$ and 10 millimoles of FOClO$_3$; the remaining portion of the apparatus is evacuated. A -196°C. bath is placed around the quartz discharge tube and around trap 1. The discharge is started producing a continuous, broad, bluish-pink band between the electrodes. Valve 1 is closed and the stopcock leading to the storage bulb is opened. Needle valve 1 is then opened slowly which permits the gas mixture to flow into the reactor, during which time valve 6 is closed. The discharge assumes a deep purple color. Needle valve 1 maintains the gas flow at a pressure drop of about 1/2 to 1" per minute as measured on gauge 1. Valve 6 is then opened so that the pressure reading on gauge 2 is about 1/2" to 1 3/4", a pressure sufficient to maintain an even flow and optimum pressure for a broad discharge. At the completion of the experiment valves 1, 2, 3, 4 and 6 are closed and the discharge is turned off. The products are then fractionated and analyzed.

Results

The reaction of difluorodiazine with fluorine perchlorate was conducted to determine whether the structure N$_2$F$_3{}^+$ClO$_4{}^-$, would form by the following reaction:

$$NF = NF + FOClO_3 \xrightarrow{SO_2} N_2F_3{}^+ClO_4{}^-$$

It was speculated that in a polar solvent fluorine perchlorate might ionize to a fluorine cation and a perchlorate anion and the fluorine cation would bond to the unshared electrons on N$_2$F$_2$.

A reaction occurred in sulfur dioxide resulting in complete decomposition of the fluorine perchlorate but most of the difluorodiazine was recovered. Volatile products consisted of NF$_3$, N$_2$O and NO$_2$. There was no evidence for the presence of the desired product, but the formation of oxides of nitrogen and NF$_3$ could conceivably have occurred by decomposition of the new product:

$$NF = NF + FOClO_3 \longrightarrow NF_2\text{-}NFClO_4 \longrightarrow NF_3 = NO_2 + ClO_2$$
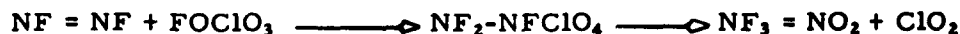
The electric discharge reaction of difluorodiazine with fluorine perchlorate is summarized in Table 52, Experiment 21.

At 25°C. fluorine perchlorate and difluorodiazine do not react but when a mixture of these gases was activated in an electric discharge a reaction occurred and nitrogen trifluoride, tetrafluorohydrazine, nitrosyl chloride and nitrogen oxides were formed. The products, NOCl, NF_3, and nitrogen oxides are typical for reactions of compounds containing labile chlorine-oxygen bonds with N-F compounds (65).

The formation of tetrafluorohydrazine is an interesting result since it could have resulted from the reaction of fluorine atoms with difluoro-diazine:

$$F - N = N - F + F \cdot \longrightarrow NF_2 - NF \xrightarrow{\quad F \cdot \quad} NF_2 - NF_2$$
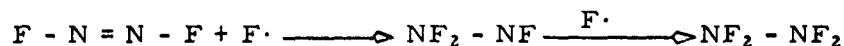
If N_2F_4 formation occurred in this manner, this would be the first example of a reaction involving saturation of the double bond in N_2F_2. It is also possible however, that some other mechanism occurred that did not involve the reaction of difluorodiazine with fluorine atoms.

It was concluded that electric discharge activation of fluorine perchlorate and difluorodiazine did not result in the formation of a new oxidizer under the conditions use. The transitory existence of the desired compound, however, could not be ruled out.

e. $\underline{FOClO_3 + F_2}$
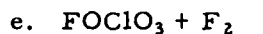
Material
F_2. The Matheson Company, Inc.

Apparatus
A 30-ml. stainless reactor equipped with a 0-1000 psig pressure gauge was attached to the standard metal high vacuum line described in Figure 28.

Procedure
The stainless steel reactor was evacuated and then filled with fluorine gas to atmospheric pressure permitted to stand for 16 hours at 25°C. to passivate the reactor.

The reactor was then evacuated and cooled to -130°C. and a measured quantity of fluorine perchlorate was added to the reactor. The reactor was then pressured to 200 psig with fluorine. The reactor was then closed and allowed to stand at 40°C. for several hours. The products were then fractionated and analyzed.

Results
The goal of this work was to determine whether $FO-ClO_3$ bond cleavage occurs when fluorine reacts with fluorine perchlorate. If the following reaction occurs

$$F_2 + FOClO_3 \longrightarrow F_2O + FClO_3$$

this would support the idea that fluorine perchlorate is a potential source of OF radicals. This knowledge would be applied in predicting new reactions with fluorine perchlorate. Normally, one would expect that fluorine perchlorate would not be a source of OF radicals due to the weak F-O bond (45.9 Kcal). Fluorine perchlorate should react to yield corresponding perchlorates rather than chlorates. Some uncertainty of the chemical reactivity of fluorine perchlorate was generated when it was observed that during the preparation of fluorine perchlorate by the reaction of fluorine with 70 per cent perchloric acid, small quantities of perchloryl fluoride (ClO_3F) formed. The ClO_3F could form by fluorination of $FOClO_3$ with the concomitant formation of F_2O:

$$F_2 + FOClO_3 \longrightarrow F_2O + FClO_3$$

Thermal decomposition of fluorine perchlorate produces as main products fluorine, chlorine and oxygen (47):

$$2FOClO_3 \longrightarrow F_2 + 4O_2 + Cl_2$$

Infrared analysis of the decomposition products does show the presence of small amounts of ClO_3F after complete decomposition at 100°C. The ClO_3F could form by several different mechanisms:

(a) fluorination of fluorine perchlorate by the elemental fluorine formed in the decomposition:

$$F_2 + FOClO_3 \longrightarrow FOF + ClO_3F$$
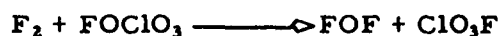
(b) fluorine perchlorate could act as a fluorinating agent for itself:

$$FOClO_3 + FOClO_3 \longrightarrow ClO_3F + Cl_2 + 1/2F_2 + 5/2 O_2$$

(c) fluorination of the transitory chlorine oxides which would result from decomposition:

$$FOClO_3 \longrightarrow F\cdot + .O. + ClO_3\cdot$$

$$F + ClO_3 \longrightarrow ClO_3F$$

When fluorine perchlorate was heated to 40°C. in the presence of fluorine at 300 psig, a reaction occurred but there was no evidence for the presence of measurable quantities of either F_2O or ClO_3F in the products. Ultraviolet examination of the gaseous products showed a single peak at 2850 Å. Fluorine monoxide has maxima at 4210, 2580, and 2940 Å(48). Infrared analysis of the gaseous mixture showed a strong band at 7.75 μ and a triplet at 12.35, 12.45, 12.60 microns. The infrared spectrum of F_2O shows strong bands at 5.75, 7.6, 8.4, 10.8 and 12.0 microns (49).

It was concluded that fluorine does not react with fluorine perchlorate to produce F_2O or ClO_3F. The products of the reaction were not identified.

f. $FOClO_3 + Cl_2C = CF_2$
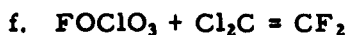
Material

$Cl_2C = CF_2$. The Matheson Company, Inc.

Apparatus

The reactor consisted of a 30- or 150-ml. stainless steel cylinder equipped with a pressure gauge. This reactor was connected to a general purpose copper tubing high vacuum line.

Procedure

In a typical experiment the stainless steel reactor was first passivated by filling cylinder with fluorine gas to atmospheric pressure.

The passivated reactor was evacuated, cooled to -130°C. and a measured amount of fluorine perchlorate condensed into the cylinder followed by the selected quantity of 1,1-dichloro-2,2-difluoroethylene ($CCl_2=CF_2$). The cylinder was closed and the reactants were slowly warmed to 25°C. by use of a succession of cooling baths (-130°C. pentane, -78°C. dry ice-acetone, -23°C., CCl_4, and 0°C.,ice). The reactants were held at 25°C. for about one hour. The products were then fractionated and analyzed.

Results

The results of several experiments are summarized in Tables 53 and 54.

In an attempt to elucidate the mode of reaction of the fluorine perchlorate molecule, with emphasis on the initial bond breaking process, its reaction with olefins was examined. Addition of fluorine perchlorate to an unsymmetrical olefin could lead to a variety of products, depending on the direction of addition. It was of interest to determine whether $FOClO_3$ could function as an OF source.

$$RRC - C - R^1 R^1 \quad \text{or} \quad RRC - CR^1 R^1$$
$$\quad\ \ | \quad\ \ | \qquad\qquad\qquad | \quad\ \ |$$
$$\quad\ \ F \quad OClO_3 \qquad\qquad O_3ClO \quad F$$

$$F - O - ClO_3 + RRC = CR^1 R^1 \longrightarrow RRC - CR^1 R^1 \quad \text{or} \quad RRC - CR^1 R^1$$
$$\qquad\qquad\qquad\qquad\qquad\qquad\qquad\ | \quad\ | \qquad\qquad\qquad\quad | \quad\ |$$
$$\qquad\qquad\qquad\qquad\qquad\qquad\qquad OF \quad ClO_3 \qquad\qquad\ O_3Cl \quad OF$$
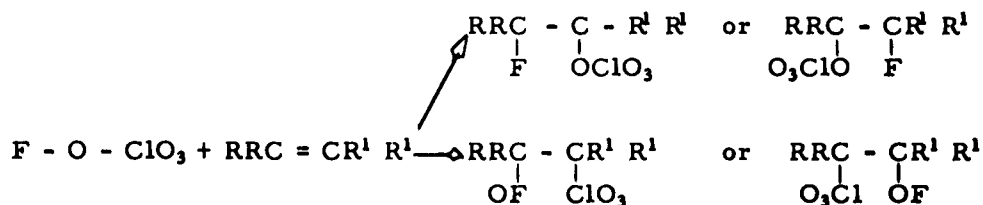
The addition of fluorine perchlorate to the olefin 1,1-dichloro-2, 2-difluoroethylene is an exothermic reaction producing a number of different products. The formation of the saturated two-carbon derivatives $CClF_2 - CCl_3$ and $CF_2Cl - CFCl_2$ as the major products in experiment 1887-63, Table 54, suggests that the initial step is the addition of fluorine followed by saturation of the radical by chlorine or chlorine substituents.

Table 53

Reaction of FOClO₃ with CCl₂=CF₂ (Formation of Unsaturated Products)

Experiment No. 1887-	Reactants FClO₄ mg.	C₂Cl₂F₂ mg.	Reactor	Temp. Range °C	Remarks and Analytical Results
-136	15	15	30 ml ss; tot.vol. with gauge 75 ml; passivated	-130 to 27	* Infrared shows disappearance of reactants with exception of FClO₃, impurity ($<5\%$). Absorption of product 7.8µ could be CF₄; 8.2 and 9.0µ right shape and location for CF₃Cl: 10.5µ (unknown)
-139	25	?	30 ml ss	25	* When the 1,1-dichloro-2,2-difluoroethylene came in contact with the fluorine perchlorate at 25°C it decomposed violently. The experiment was discontinued
-140	25	25	30 ml ss	-130 to 25	* Infrared analysis of products obtained after warming mixture to 25°C. System recooled to -130°C and infrared spectra obtained of volatile fractions at -130°C: -78 to -50°C and 25°C. Absorptions at 5.5µ; 7.6 -8.0-8.1, 9.4 attributable to C₂ClF₃. Absorptions at 6.2µ, 8.5µ; 10.1µ and 11.7µ (triplet) attributable to C₂Cl₃F. also unknown complex absorption in CF and C-Cl area
-149	60**	130	30 ml ss	-130 to 25	* Infrared spectra of products complex Absorptions present previously attributable to C₂ClF₃ and C₂Cl₃F(exp. 1887-140) also unreacted C₂Cl₂F₂ and other unknown bands Mass spec analysis - mainly unreacted C₂Cl₂F₂ and evidence of ions CF₃; CCl₂CF₂; and CF₂Cl⁺ present.

* FClO₄ purified and infrared spectra taken prior to each experiment. Also, standard spectra for 1,1-dichloro-2,2-difluoroethylene at various pressures were obtained.

** Not all FClO₄ condensed due to formation of noncondensables when it was distilled into reactor.

Table 54

Reaction of FOClO₃ with CCl₂=CF₂

Exp. No. 1887-63

(-130°C to 25°C)

Product Analysis (0.603 g FOClO₃; 0.608 g CCl₂CF₂)

Analyses	Volatile at -130°C 0.180 g	Volatile at -78°C 0.187 g	Nonvolatile at -78°C 0.844 g
Mass Spectrometry [a]	CF_4 +++ CO_2 ++++	CF_2Cl_2 + CF_4 + $FClO_4, FClO_3$ + CO_2 ++++ $COCl_2$ [b] + COF_2 [c] +	CF_2Cl-CCl_3 ++++ CF_2Cl-CCl_2F ++ CO_2 [b] ++++ $COCl_2$ [b] ++ CF_3Cl ++ Mass 97 trace
Infrared	Essentially CF_4	$FClO_3$, 7.6; CCl_3F, 9.1, 10.7; CCl_3F, 9.1, 11.8; Evidence for $COCl, COF$. CF_2Cl-$CFCl_2$	CF_2Cl-CCl_3, 8.5, 9.6, 11.7, 12.6; CF_2Cl-$CFCl_2$, 8.5, 9.0, 9.6, 11.0; Absorption at 5.3 suggests COF Absorption at 5.5 suggests COCl
NMR			No low field peaks-absence of -OF All peaks appear between +65 ppm + 82 ppm (Freon 11) Majority of sample (70%) is CF_2Cl-$CFCl_2$ and CF_2Cl-CCl_3 No CF_3-CF_2X present No unsaturation
VPC		One major low boiler trace two other components	

(a) Mass spectrometry: + signifies relative proportions
(b) or some other compound containing the COCl group
(c) or some other compound containing the COF group

1) $CF_2 = CCl_2 + F-OClO_3$ ⟶ $\dot{C}F_2 - CCl_2F + ClO_4\cdot$

2) $ClO_4\cdot$ ⟶ $Cl\cdot + 2O_2$

3) $\dot{C}F_2 - CCl_2F + Cl\cdot$ ⟶ $CF_2Cl - CCl_2F$

4) $2Cl\cdot$ ⟶ Cl_2

5) $CF_2 = CCl_2 + Cl_2$ ⟶ $CF_2Cl - CCl_3$
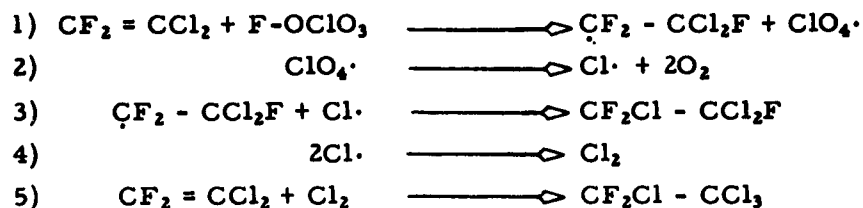
In experiments 1887-140 and 1887-149, Table 53, the major products appeared to be $CCl_2 = CClF$, and $CF_2 = CFCl$ on the basis of infrared analysis. The infrared spectrum of $CCl_2 = ClF$ is shown in Figure 31. The infrared spectrum of the product obtained in experiment 1887-140, $CF_2 = CCl_2$ is shown in Figure 33.

In Figure 31, the bands at 5.5, 7.6, 6.8, 8.0, 8.1 and 9.4 microns suggest $CF_2 = CFCl$ and absorptions at 6.2, 8.5, 10.1 and the triplet at 11.5, 11.65 and 11.70 microns indicate $CFCl = CCl_2$. This indicates that either disproportionation of the starting olefin occurred or that addition followed by elimination has taken place. A disproportionation reaction involving vinylic halides is very unlikely and reactions of this kind have not been reported:

$$CF_2 = CCl_2 \ \xrightarrow{\ \ /\!\!\!\!\!\!\ } \ CFCl = CCl_2 + CF_2 = CFCl$$
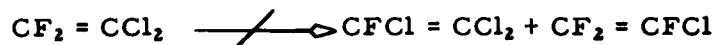
A more reasonable possibility is that the intermediate radicals which form can either eliminate a halogen radical, or react further to give saturated products as described earlier. The elimination of chlorine atoms is a reasonable postulate, but the formation of the monofluoro olefin by fluorine atom

$$\dot{C}F_2 - CCl_2F \ \longrightarrow \ CF_2 = CFCl + Cl\cdot$$

$$CF_2Cl - \dot{C}Cl_2 \ \longrightarrow \ CFCl = CCl_2 + F\cdot$$
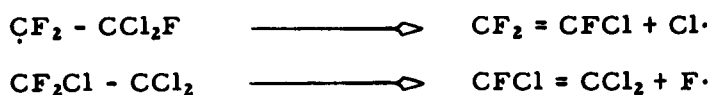
elimination is less satisfactory. At the present time no satisfactory explanation for the formation of trichlorofluoroethylene can be given. The absence of two-carbon CF_3 derivatives indicates either that the addition of chlorine atoms to the olefin does not occur or, more probably, that the addition is selective in a direction opposite to that found for fluorine.

6) $CF_2 = CCl_2 + Cl\cdot$ ⟶ $CF_2Cl - \dot{C}Cl_2$

7) $CF_2 = CCl_2 + Cl\cdot$ ⟶ $\dot{C}F_2 - CCl_3$
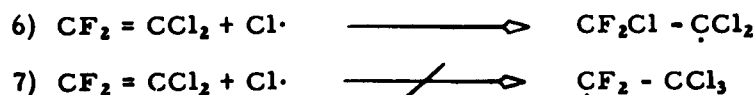
If reaction did occur one would expect some CF_3-CCl_3 to be produced. The absence of such a product suggests that chlorine addition occurs at the less sterically hindered carbon atom; fluorine addition appears to occur in the manner expected, as based on the polarization of the double bond. No evidence for the formation of OF compounds was obtained and it is doubtful that any significant addition of OF radicals occurred from $FO-ClO_3$ bond cleavage. This could be due to the absence of such bond breaking or to the instability of the OF radical before addition occurred. Since the initial addition to the olefin is not expected to occur by preliminary decomposition

Figure 31

Infrared Spectrum of Reaction Product from FOClO$_3$ with CF$_2$CCl$_2$ (Exp. -149)
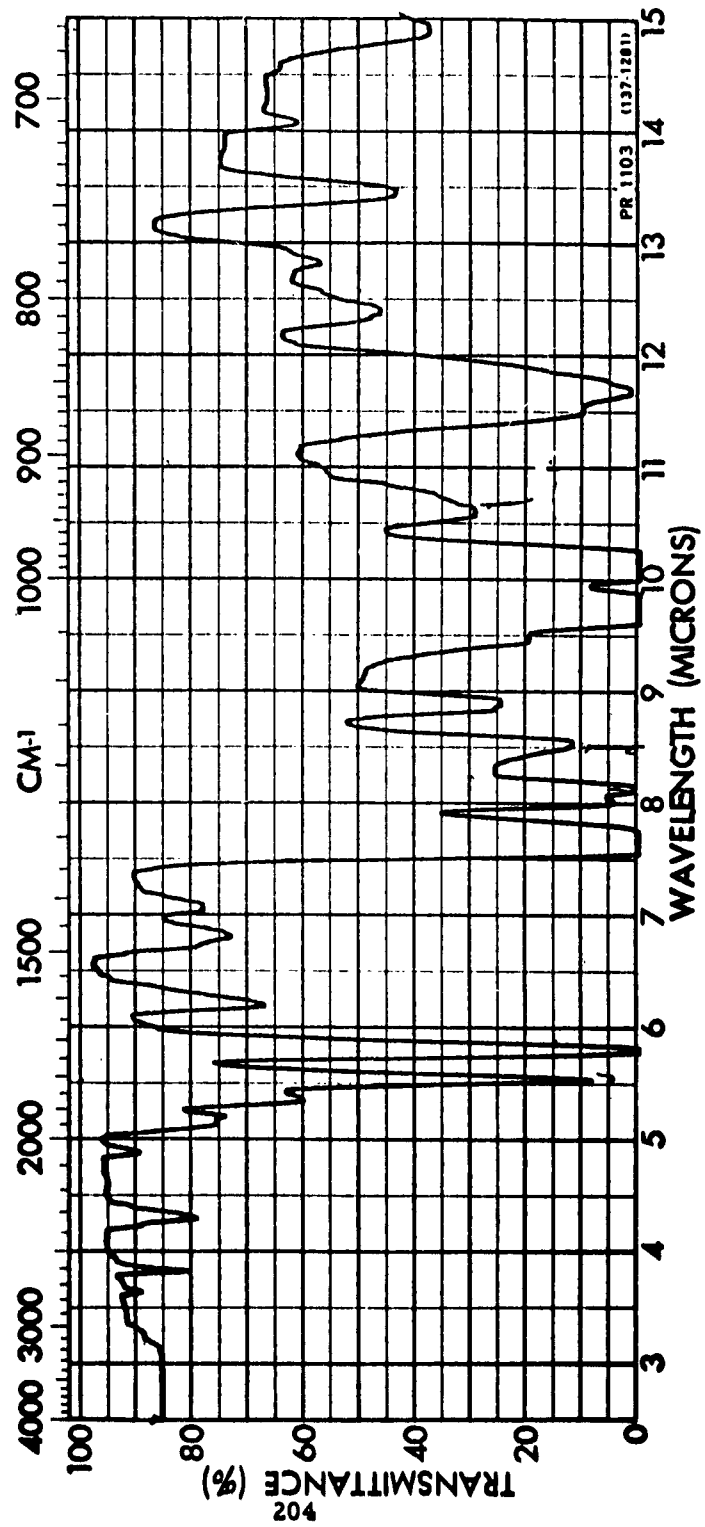
Figure 32

Infrared Spectrum of Reaction Product from $FOClO_3$ with CF_2CCl_2 (Exp. -140)
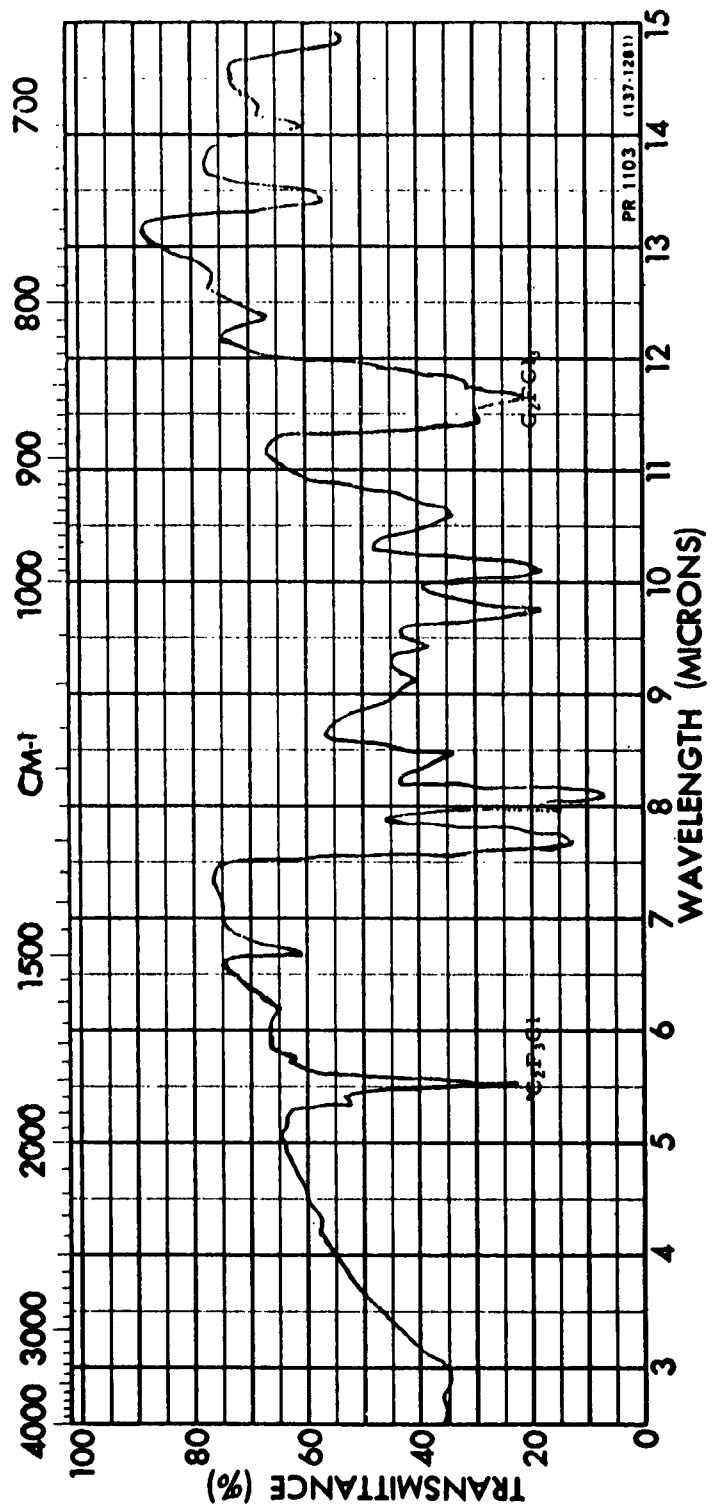
Figure 33

Infrared Spectrum of 1,1-Dichloro-2,2-Difluoroethylene
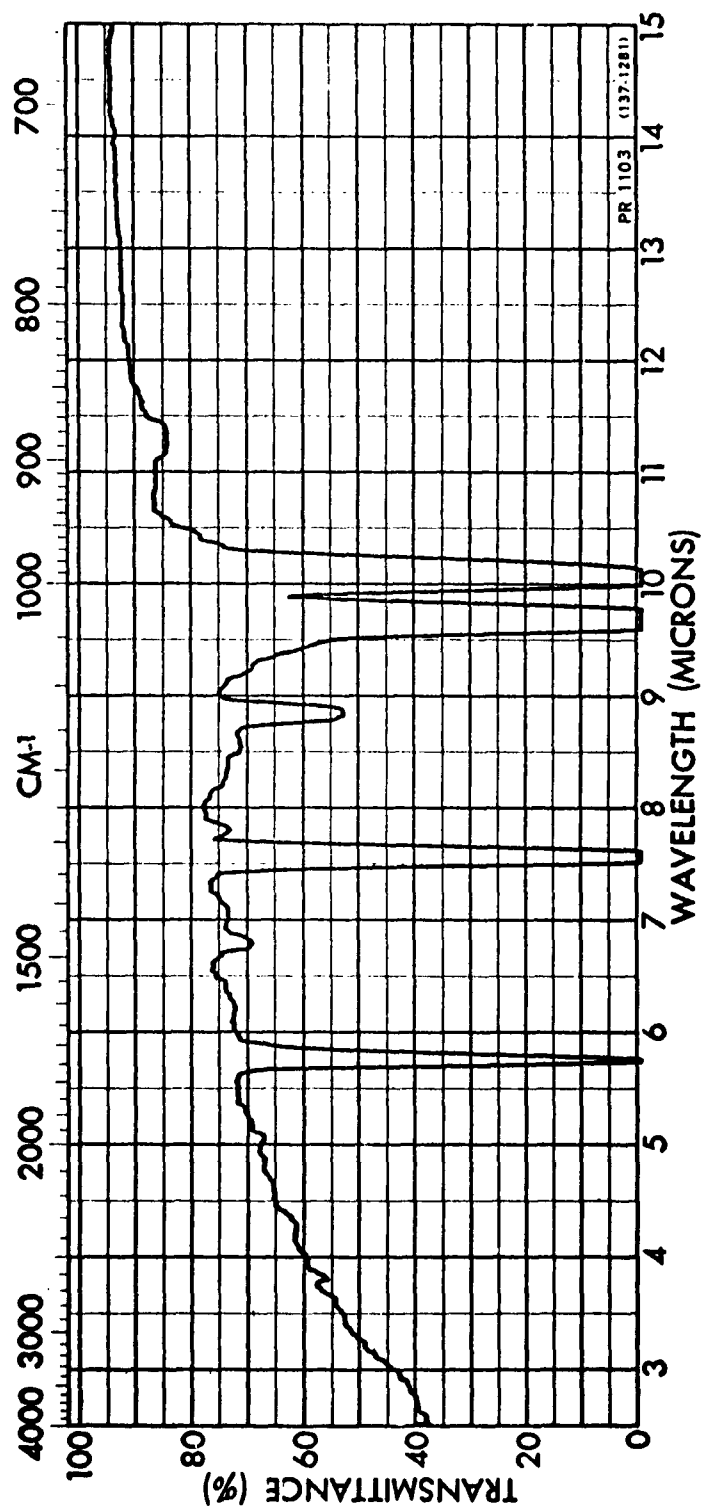
of the $FOClO_3$ into radicals, the absence of OF products suggests that the molecular addition of $FOClO_3$ results in abstraction of fluorine.

The presence of one-carbon cleavage products such as CCl_3F, CCl_2F_2, CF_4, CF_3Cl, F_2CO, Cl_2CO and CO_2 probably stems from oxidation of the olefins and initial radicals ($CF_2Cl - CCl_2$, CF_2; CCl_3) to produce the chloro and fluorophogenes. These materials could then disproportionate to produce

$$CF_2 = CCl_2 + O_2 \longrightarrow COF_2 + COCl_2$$

the wide variety of substituted fluoro and chloromethanes found. Reactions

$$2F \overset{O}{\underset{\|}{C}} F \longrightarrow CF_4 + CO_2$$

and

$$2F \overset{O}{\underset{\|}{C}} Cl \longrightarrow CF_2Cl_2 + CO_2$$
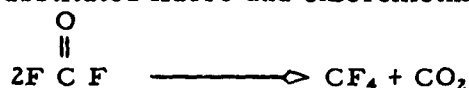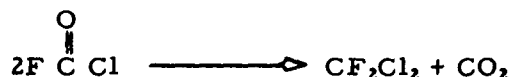
of this kind have been noted by other investigators (50, 51).

This work indicated that reactions with fluorine perchlorate involve breaking of the weak O-F bond ($F \dotplus OClO_3$) rather than the O-Cl bond ($F \cdot O \dotplus ClO_3$). The reaction of fluorine on fluorine perchlorate (Section V, A, 1, e) also supported this hypothesis.

g. $FOClO_3 + ClF_3$

Material

ClF_3. The Matheson Co., Inc.

Apparatus

The reactor consisted of a 100-ml. stainless steel cylinder which was connected to a general purpose copper tubing high vacuum line. In some experiments a 100-ml. Pyrex glass reactor was used.

Procedure

In a typical experiment the reactor was connected to the metal high vacuum line and evacuated and cooled to -130°C. A measured amount of chlorine trifluoride was then condensed into the cylinder followed by the addition of fluorine perchlorate. The reactor was then closed and the reactants were held for 1-20 hours at 25°C. The products were then fractionated and analyzed.

Results

One hypothetical compound that is especially attractive, based on specific impulse calculations using lithium and polyethylene fuel, is ClO_4ClF_4. The calculated impulse is 303 seconds.

Since tetrafluorochlorate salts such as $KClF_4$ were prepared by the dissolution of various metal fluorides in chlorine trifluorides, it was thought that an analogous reaction might occur with fluorine perchlorate to give the desired compound ClO_4ClF_4, i.e:

$$2ClF_3 \rightleftharpoons ClF_2^+ + ClF_4^-$$

$$KF \rightleftharpoons F^- + K^+$$

$$2ClF_3 + KF \longrightarrow KClF_4 + ClF_3$$

$$2ClF_3 \rightleftharpoons ClF_2^+ + ClF_4^-$$

$$FClO_4 \rightleftharpoons F^- + ClO_4^+$$

$$2ClF_3 + FClO_4 \longrightarrow ClO_4^+ClF_4^- + ClF_3$$
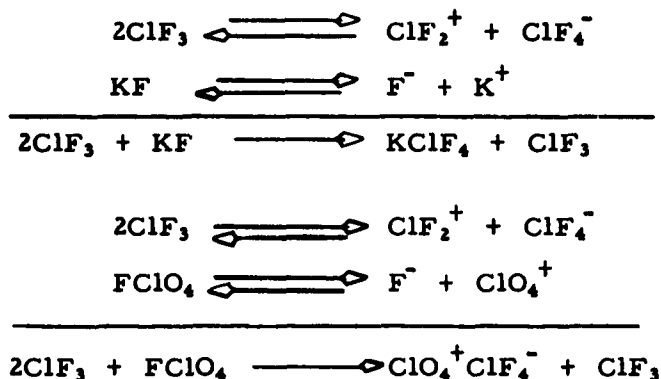
For an ionic aggregation, the structure would be expected to be a lattice type material containing ClO_4^+ and ClF_4^- ions. For a covalent structure, one can visualize ClO_4ClF_4 in which the unshared pair of electrons of the ClF_4^- ion has been donated to one of the oxygens of the perchlorate ion.

The results of several experiments are summarized in Table 55.

The first experiment was performed in a glass reactor at room temperature using approximately equimolar quantities of the two reagents. At the end of a three-hour reaction period there was no evidence for reaction, other than some etching of the glass.

In designing the experiments it was planned to follow the reaction by changes in pressure. Since both reagents are gases, if the desired reaction product also were a gas, one would expect that an equimolar mixture would lead to a 50 per cent decrease in pressure. If the final material proved to be a liquid or solid, there would be a greater pressure reduction.

In the first experiment there was no significant pressure decrease, which also led to the conclusion that the desired reaction had not taken place. Infrared examination of the products indicated some silicon tetrafluoride, which was expected after noting the attack on the glass.

The molecular weight of the gaseous mixture at the end of the experiment also was measured as a means of establishing reaction. The molecular weights of the reagents are, $FClO_3$, 118.5, and ClF_3, 92.5, while that of ClO_4ClF_4 is 211.0. The observed molecular weight was determined as 86.6, which is indicative of the fact that no ClO_4ClF_4 formed. This value of 86.6, which is below the molecular weight of either component, indicates some decomposition to lower molecular weight products.

Because of the attack on the glass in the first experiment, the reactor

Table 55

Reactions of $FClO_4$ with ClF_3

Expt. No.	Reactor	Reactants (Millimoles) $FClO_4$	ClF_3	Temp. (°C)	Time (hrs.)	Millimoles after Reaction	Ratio of Initial to final No. of Millimoles	Molecular Wt. of Products	Infrared Analysis of products	Remarks
1	glass	1.19	1.34	24	3	2.51	0.992	86.6	SiF_4, $FClO_4$	Reactor etched
2	glass, coated with Teflon	0.14	1.04	100	1	1.93	1.64	-	-	Teflon flaked off reactor
3	steel	1.50	1.51	26 110	19 2	7.35	1.76 2.44	53.7	$FClO_4$ (very low)	Explosion in reactor
4	steel	1.62	1.62	25	20	8.29	2.56	47.9	$FClO_4$ (very low) ClF_3 low	Explosion in reactor

was coated by spraying the interior with Teflon[*]. In experiment number 2, a temperature of 100°C. was reached over a period of one hour. The number of millimoles increased from an initial 1.18 to 1.93, indicating decomposition rather than combination. However, no violent reaction could be detected. Because the Teflon tended to flake off the glass, particularly on the curved portions of the reactor (which might have led to decomposition), the glass reactor was abandoned and a steel cylinder was employed in the remaining experiments.

Experiment number 3 was conducted with equimolar amounts of $FOClO_3$ and ClF_3. These ingredients were maintained at 26°C. for nineteen hours and then opened to the vacuum system for examination. At this instant a vigorous reaction took place, producing a loud noise, but doing no damage. A pressure measurement indicated that 5.31 millimoles of gas were now present instead of the original 3.01. This represents a 1.76-fold increase in the number of moles of gas. Had complete decomposition occurred, according to

$$ClF_3 + FOClO_3 \longrightarrow Cl_2 + 2F_2 + 2O_2$$

the factor would have been 2.5. This suggested unreacted starting material was still present and the experiment was continued with the temperature being increased to 110°C. for two more hours. The millimoles present after that time was 7.35 or a ratio of 2.44 over the initial value. This indicates that practically complete decomposition had taken place.

Infrared examination of the final gas mixture showed only a slight amount of $FOClO_3$ remaining. The average molecular weight of the gases was 53.7, approaching that for complete reversion to the elements.

Experiment 4 was performed using equimolar quantities of ClF_3 and $FOClO_3$ and allowing the mixture to stand in the steel cylinder for twenty hours at 25°C. As the cylinder was opened to the vacuum system another vigorous reaction took place accompanied by a loud noise. The number of moles of gas had increased by a factor of 2.56 and the average molecular weight was 47, again suggesting complete decomposition. Infrared examination of the gases showed only small amounts of ClF_3 and $FOClO_3$ remaining.

There is no obvious explanation for these violent decompositions. The reactor, itself, was treated twice with chlorine trifluoride prior to the admission of the fluorine perchlorate. This, in conjunction with the fact that the decomposition took place after both reagents were in the system, should preclude the possibility that grease or other impurities had initiated the reaction.

A possible explantion is the free radicals such as $F\cdot$, $ClO_4\cdot$, $FO\cdot$ or $ClO_3\cdot$ might have formed and initiated a chain reaction. No evidence, however, for such a phenomenon was noted in the glass system.

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[*] "Fluoro Glide", Chemplast, Inc., East Neward, N.J.

It is also possible that the rapid decomposition of fluorine perchlorate could have been initiated by the mechanical action of the gas molecules passing rapidly through the reactor orifice. However, no such phenomenon was noted when the glass reactor was used nor when samples of the material passed through other valving systems.

The reaction of fluorine perchlorate with chlorine trifluoride was also investigated using Freon-11 as a solvent in a reactor constructed of Kel-F. At 25°C. there was no evidence of a reaction and the reactants were recovered.

It was concluded that the reaction of fluorine perchlorate with chlorine trifluoride results only in the formation of low molecular weight decomposition products in the absence of a solvent. In Freon-11, there is no reaction at 25°C.

h. $FOClO_3 + N_2H_4$
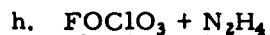
Material

N_2H_4. Olin Mathieson Chemical Corporation. Anhydrous.

Apparatus

The reactor consisted of a 75-ml. Pyrex vessel which was attached to a general purpose metal high vacuum line equipped with a pressure gauge.

Procedure

A known quantity of anhydrous hydrazine is placed in the 75-ml. glass reactor containing a magnetic stirring bar, and the reactor is cooled to -78°C. and evacuated. Approximately 10 ml. of Freon -11, distilled from phosphorus pentoxide, is condensed into the reactor. The system is warmed to room temperature, vigorously stirred and slowly cooled to 0°C. before being cooled to -78°C. This insures better dispersal of the insoluble hydrazine (f.p. 1°C.). A known quantity of fluorine perchlorate is then condensed into the reactor and after a period of about 0.5 hour the system is warmed slowly to room temperature. Pressure is recorded during this period, the reactor is then recooled to -78°C. and gas samples removed for analysis. The liquid remaining is then distilled. In general, a small amount of white solid along with a yellow viscous liquid, which is the major product, remain on removal of the Freon-11. The liquid is higher boiling than the Freon-11. Characterization is conducted by elemental and instrumental analyses and further separation of the liquid, if necessary, is conducted by vacuum distillation.

Results

The reaction of anhydrous ammonia with perchloryl fluoride, reported by Engelhecht and Atzwanger (52) results in the formation of the ammonium salt of perchlorylamide
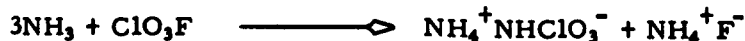
$$3NH_3 + ClO_3F \longrightarrow NH_4^+NHClO_3^- + NH_4^+F^-$$

The reaction of hydrazine with fluorine perchlorate was investigated

to determine whether a similar reaction would occur to form new hydrazine perchlorates such as:

$$N_2H_4 + FOClO_3 \longrightarrow (N_2H_5)^+(N_2H_3OClO_3)^-$$

The results of several experiments are summarized in Table 57.

The reaction of hydrazine with fluorine perchlorate results in the formation of a yellow viscous high boiling liquid as the major product, Surprisingly, very little solid product formed and only in experiment 1691-82 was sufficient solid produced to enable a separation to be made. X-ray analysis of the solid was unsatisfactory because of the lack of standards for hydrazine salts. In general, the reaction produced a small quantity of non-condensable gas which was assumed to be nitrogen. The initial liquid product which forms was found to contain hydrazine hydrate, due apparently to the formation of water from the initial reaction. None of the products showed any oxidizing properties with respect to neutral or acidic potassium iodide solutions. The infrared spectra suggested the presence of hydrazine salts in the high boiling liquid. Mass spectrographic analysis of the liquid, using a heated inlet which caused decomposition, indicated the presence or formation of HCl, N_2H_4, and SiF_4. NMR examination generally was unsatisfactory with the exception of the product obtained in experiment-79, from which a signal indicating the presence of one type of hydrogen was obtained. No fluorine signal could be received although there was present 4.9 per cent fluorine. From the product obtained in experiment-82 no fluorine or hydrogen signals could be detected.

The products obtained from this reaction were not characterized sufficiently to permit firm conclusions but the absence of any material which would oxidize potassium iodide was an indication that the system did not produce a new oxidizer. The formation of a liquid product suggests that several hydrazine salts may have formed such as the fluoride, chloride and perchlorate, which could exist as low melting mixtures.

i. $FOClO_3 + NH_3$

Material
NH_3. The Matheson Cu., Inc. Anhydrous, purity $99^+\%$.

Apparatus
These experiments were conducted in Pyrex glass reactors which were attached to a general purpose metal high vacuum line equipped with a pressure gauge.

Procedure
The procedure was varied for specific experiments and these changes are noted in Table 56. In a typical experiment, 0.3 g. $FOClO_3$ and 0.1 g. ammonia were dissolved in Freon-11 in a Pyrex reactor cooled to -78°C. The reactants were held for 5 hours at -60°C. The products were then fractionated and analyzed.

Table 57

Reaction of FClO$_3$ with N$_2$H$_4$

| Experiment No. | Reactants | | | | Analyses and Comments | |
| | Solvent Freon - 11 | | | | | |
	FClO$_3$ g.	mm	N$_2$H$_4$ g.	mm	Gas Products	Liquid
1691-73	0.12	1.0	0.3	9.4	Overhead gas - Freon-11	Yellow viscous liquid; I.R. absorptions at 3.0 to 4.5μ (w); 6.2 - 6.6μ (w)
1691-76	0.2	1.7	0.5	15.6	C -23 and -78 Freon-11 and unknown absorption at 8.8 and 8.9μ (ClO region)	Volatile material - I.R. hydrazine hydrate High boiling liquid I R - 3.5μ, 6.2-6.4μ, 7.4μ, 8.9 - 9.4μ, 10.5μ %F = 2.52
1691-79	0.103	0.87	0.55	17.1	-196 Noncondensable gas 25°C - IR Freon-11 0.036 gms.	Volatile liquid 0.4443 g. - I.R. hydrazine hydrate and hydrazine; NMR - one type of hydrogen, no fluorine signal. High boiling liquid, 0.1650 g. Similar to Exp.76 %F = 4.9, %Cl = 14.63. NMR - No fluorine signal. One type of hydrogen present
1691-82	.464	3.9	.48	15.1	Volatile liquid. I.R. - hydrazine hydrate and hydrazine	High boiling liquid 0.55 gms. NMR No For H signal %F = 6.5; %Cl = 5.0 (probably low) %N = 14.4. I.R. same as above Decomposition temperature = 150°C in air Solid product 0.050 gms. X-ray pattern unknown

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Results

Engelbrecht and Atzwanger (52) reported that perchloryl fluoride reacts with anhydrous ammonia to yield the ammonium salt of perchlorylamide by the following reaction:

$$3NH_3 + ClO_3F \longrightarrow NH_4^+NHClO_3^- + NH_4^+F^-$$

It was speculated that a similar reaction might occur with fluorine perchlorate:

$$3NH_3 + FOClO_3 \longrightarrow NH_4^+(NHOClO_3)^- + NH_4^+F^-$$

Since polarization and bonding in $FOClO_3$ are different from that in ClO_3F, products reflecting $FO-ClO_3$ cleavage and $F-ClO_3$ cleavage may also form in which OF or F are displaced as postive ions, i. e.:

$$NH_3 + FO - ClO_3 \longrightarrow HClO_3 + NH_2OF$$

$$NH_3 + F - OClO_3 \longrightarrow NH_3F^+ClO_4^-$$
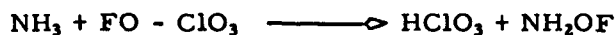
The results of several experiments are summarized in Table 56.

The reaction of ammonia with fluorine perchlorate results in the formation of solid crystalline materials. No indication of the formation of volatile materials was obtained except in experiment 387407 where a trace quantity of NF_3 was shown to be present from infrared analysis of the overhead gases. No evidence for the formation of NF_3 was found in later experiments.

The solid product was predominantly ammonium perchlorate. The X-ray diffraction pattern (powder) indicated ammonium perchlorate plus several unknown lines. The unknown lines wre compared to the standard patterns of ammonium fluoride, ammonium bifluoride, and ammonium chloride but the lines could not be identified. Infrared examination of the solid was attempted with mulls containing Nujol, Kel-F and fluorocarbon oil. The absorption peaks were those expected for ammonium perchlorate along with a slight broadening of the NH absorption band at 3.0μ and an unknown absorption in the 13.9μ region. The broadening at 3μ could be due to the presence of a second ammonium salt and the band at 13.9 might be due to $SiF_6^=$ absorptions.

The solid was soluble in water and insoluble in nitromethane and acetone. It did not oxidize acidic or neutral solutions of potassium iodide. The pH of the water solution was 4-5 and the material partially decomposed to $(NH_4)_2SiF_6$ when the solution was heated.

An effort to separate the ammonium perchlorate from the other materials by preferential solubility in liquid ammonia was not successful. The X-ray pattern of the ammonia-soluble portion was similar to that of the original material except for the presence of strong amorphous scattering.

The elemental analyses were not particularly helpful in defining the products more exactly. In experiment 387409 a chlorine value of 24.6 per

Table 56

Reaction of FOClO₃ with NH₃

Exp. No.	Reactants Solvent - Freon 11 FClO₃ g.	Mn. g.	NH₃ Mn. ml.	Temp. °C	Reaction time-hrs.	Solid Product Analysis	Remarks
387407	0.48	4.0	0.14 8.0	-78° to -63°	5	I.R. and X-ray identify NH_4ClO_4 plus unknown absorptions - see 1691-71	Trace NF_3 found in gaseous products. Solid was stable to >250°C
387409	0.25		0.12	-78° to -63	5	%N =15.9;%F=12.8;%Cl=24.6 IR-Nujol mull-NH_4ClO_4 X-ray NH_4ClO_4 - See 1691-71	X-ray of solid shown unknown lines not due to NH_4F,$NH_4F\cdot HF$, or NH_4Cl
1691-60	0.27	2.3	6.9	-78°	1.5	Only trace of solid product	
1691-68	.12	1.0	0.06 3.7	-78° to -60		%F=10.5 total;%F=7.5(fluoride) X-ray - NH_4ClO_4 + unknown lines; see 1691-71	I.R. strong NH at 3μ; broadness between 3-4μ may be due to HF complex; doublet near 7μ probably NH_4^+; ClO_4^- at 9.3-9.5μ .Absorption at 13.9μ may be SiF_4.
1691-71	0.13	1.1	0.06 3.7	-78° to -63		20.87% NH_3 on basic hydrolysis %F=9.63. X-ray -NH_4ClO_4 plus unknown lines. IR 3.5 (s), 3.65(shoulder) 5.0,5.5,6.95(s). 7.3(s),7.5(w),9.3(m),9.5(m), 10.3(w), 13.9(s). X-ray lines (A) in addition to those due to NH_4ClO_4: 10.5, 5.40, 4.75, 3.76, 3.07, 2.65, 2.13, 1.97, 1.32	No change in X-ray pattern on dissolving part of solid in liquid ammonia except for additional amorphous pattern in ammonia fraction. Collected 0.127 gms. solid.
1691-63	Flow system - N₂ carrier diluent 0.13	1.5	0.03 1.5	-78	0.7	%N = 16.38	Solid formed in very thin film along sides of reactor.
1691-66	0.12	1.4	0.14 8.0	-78	0.8		Slight amount of solid formed
1691-67 no solvent	0.10		8.0	-130 to -78	30 min. at -130°		Detonation occurred when reactants were warmed to -78°C. No reaction noted at -130°C.

cent would, if we assume the chlorine is present only as ammonium perchlorate, give a nitrogen-fluorine ratio of 1.52 for the remaining unknown material. The ammonium perchlorate would amount to 81 per cent of the sample on this basis. In experiment 1691-68 an analysis for total fluorine gave a value of 10.5 per cent, but titration of a water solution of the sample gave a value of only 7.5 per cent. This difference of three per cent reflects fluorine bound in the product in some form other than as fluorine ion.

At the present time it is not possible to satisfactorily indicate all the products of the reaction. If fluoramine forms, it would be expected to decompose in the presence of ammonia to hydrazine and hydrogen fluoride or react further to produce difluoramine and finally nitrogen trifluoride. These possibilities may be summarized by the following equations:

$$(1) \quad NH_3 + FOClO_3 \longrightarrow NH_2F + HClO_4$$

$$(2) \quad HClO_4 + NH_3 \longrightarrow NH_4ClO_4$$

$$(3) \quad NH_2F + FOClO_3 \longrightarrow HClO_4 + NHF_2$$

$$(4) \quad NHF_2 + FOClO_3 \longrightarrow HClO_4 + NF_3$$

$$(5) \quad NH_2F + NH_3 \longrightarrow N_2H_4 + HF$$

$$(6) \quad NHF_2 \longrightarrow N_2F_2 + HF$$

$$7) \quad NH_3 + HF \longrightarrow NH_4F \xrightarrow{HF} NH_4F \cdot HF \xrightarrow{HF} NH_4F \cdot 2HF$$

$$8) \quad N_2H_4 + HF \longrightarrow N_2H_5F$$
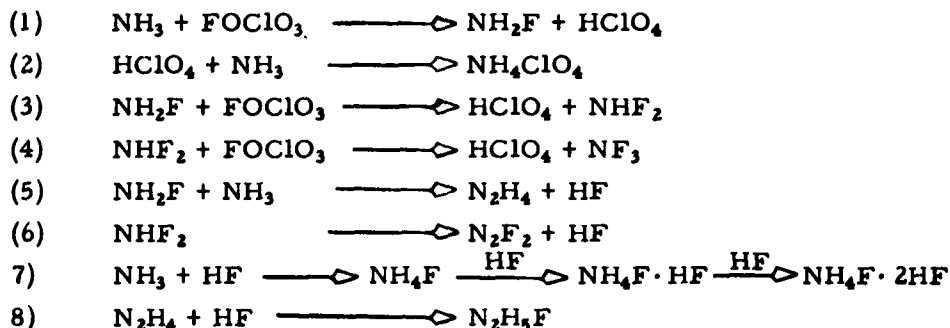
The inert character of the solid to neutral or acidic potassium iodide suggests the absence of a new oxidizing component in the solid. The formation of trace quantities of NF_3 found in one experiment suggest that fluoramine and difluoramine may be intermediates. The inability of X-ray analysis to positively identify ammonium fluoride or bifluoride as being present is difficult to explain since hydrogen fluoride appears to be present in some complexed form. The presence of hydrazine hydrofluoride has not been established but it may very well be present. The presence of the known $NH_4F \cdot 2HF$ or $(NH_4)F \cdot (NH_4)_2SiF_6$, whose X-ray patterns were not available, would also be an explanation of the unknown lines. The presence of fluorine which does not directly produce fluoride ion on solution in water is probably due to the presence of $SiF_6^=$, resulting from reaction with the glass. Work on this reaction was suspended when it appeared that NH_4ClO_4, NH_4F complexed with HF and possibly N_2H_5F along with some $(NH_4)_2SiF_6$ were the only solid products of this reaction.

j. $FOClO_3 + BF_3$
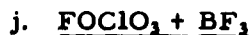
Material

BF$_3$. The Matheson Co., Inc.

Apparatus

The reactor consisted of a 6'' length of Teflon tubing closed at one end and attached to a metal high vacuum line. The pressure gauge and metal lines of the high vacuum line were passivated by treatment with fluorine gas for 16 hours followed by a similar treatment with boron trifluoride.

Procedure

In a typical experiment fluorine perchlorate was condensed into the reactor at -130°C. The reactor was then warmed to 25°C. and the pressure recorded. An equivalent quantity of gaseous boron trifluoride was then added so that the total pressure at 25°C. was double the starting pressure of fluorine perchlorate. The pressure of the system was then recorded at several temperatures as the reactor was cooled to -78°C. and then to -130°C. Samples were taken at various temperatures for infrared examination. At -130°C. the boron trifluoride was vacuum distilled from the mixture leaving behind the fluorine perchlorate.

Results

Fluorine perchlorate is sensitive to shock and thermally unstable at temperatures above 25°C. There were no known complexes of fluorine perchlorate so that stabilization or incorporation of this oxidizer in a non-cryogenic system was not feasible. Exploratory studies were undertaken to determine whether the strong Lewis acid, boron trifluoride, would form a stable complex with fluorine perchlorate:

$$BF_3 + FOClO_3 \rightleftharpoons F_3B : O_3ClOF$$

Knowledge of complex formation was expected to be useful information which could be applied to predicting the chemical behavior of fluorine perchlorate in exploratory reactions designed to form new oxidizers.

When fluorine perchlorate was added to boron trifluoride in a Teflon reactor, there was no evidence of a reaction.

The calculated pressure of the mixture at -78°C. and at -130°C. (assuming ideal behavior) was compared to the observed pressure readings. Although the differences between the calculated and observed pressures were small they were greater than the experimental errors in the determination. For a mixture containing 2.4 inches of fluorine perchlorate and 2.6 inches of boron trifluoride at 25°C. the pressure recorded at -78°C. was 3.6 inches. The calculated pressure is 3.9 inches (2.6 inches BF_3 + 1.3 inches $FOClO_3$). This decrease of 0.3 inches may be attributed either to the formation of a weak complex between the two components or to the solubility of boron trifluoride in the liquid fluorine perchlorate at -78°C. When the temperature was reduced to -129.7°C. the pressure dropped to 1.6 inches. The reported vapor pressure of liquid boron trifluoride at this temperature is 2.2 inches (53) so that a significant decrease of 0.6 inches was noted. Fluorine perchlorate has no significant vapor pressure at this temperature. It was not possible to conclude whether the observed decreases were due to the formation of a weak complex between the two components or

were the result of the solubility of fluorine perchlorate and boron tri-
fluoride in the liquid phases present. Infrared examination showed only
BF_3 in the gas phase at -130°C. and both components present at -78°C.
Vacuum distillation of the mixture at -130°C. led to the complete
removal of the BF_3 and the quantitative recovery of the $FOClO_3$. Further
work in this area was suspended since complex formation, if any, was
negligible under ambient conditions.

B. Reactions with $FClO_3$

1. Objective

In most instances, when compounds containing labile oxygen and N-F
intermediates such as N_2F_4, NF_2H or NF_2Cl were reacted, extensive
decomposition to nitrogen oxides occurred. Yet, in reactions involving
perchloryl fluoride, some vigorous activation was necessary since this
compound is very stable and does not react readily.

The use of perchloryl fluoride as a reactant posed several advantages.
First, the compound was available commercially in high purity, therefore,
complicated and expensive laboratory preparations were eliminated.
Secondly, its structure presented the possibility of splitting out a stable by-
product to provide the driving force for the proposed reactions:

$$NF_2-NF_2 + F-ClO_3 \longrightarrow NF_2ClO_3 + NF_3$$

The inherent stability of perchloryl fluoride, however, was a dis-
advantage since it was necessary to use highly energetic conditions to
promote reactions and these same conditions were likely to cause the
desired products, such as NF_2ClO_3, to decompose.

Possible complex formation, or reaction, with both BF_3 and NF_3,
also was investigated.

a. $FClO_3 + BF_3$

Material

    $FClO_3$. Pennsalt Chemical Company, purity 99%.

    BF_3. The Matheson Company, Inc.

Apparatus

    The nickel reactor used in this experiment is described in Figure 2.

Procedure

    The reactor was cleaned and attached to a metal vacuum transfer line.
The reactor was then evacuated, cooled to -196°C., and 0.166 g. of BF_3
condensed into the reactor followed by the addition of 0.219 g. of $FClO_3$.
The reactor was closed and the reactants were agitated for 24 hours at
200°C. The products were then fractionated and analyzed.

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Results

The purpose of this experiment was to determine whether a reaction occurs between boron trifluoride and perchloryl fluoride to form perchloryl tetrafluoroborate,

$$FClO_3 + BF_3 \longrightarrow ClO_3^+ BF_4^-$$

The results of this experiment are summarized in Table 8, Experiment 1876D-96.

There was no evidence of a reaction. The reactants were recovered and identified by infrared analysis.

(b) $FClO_3 + N_2F_4$
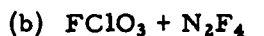
Material

$FClO_3$. Pennsalt Chemical Co., purity 99%

N_2F_4. Prepared by the reaction of NF_3 + Hg as described in Section X.

HSO_3F. Allied Chemical and Dye Corp. Distilled before use.

Apparatus

This experiment was conducted in the microwave discharge apparatus described in Figure 34. The reaction tube was initially made of Teflon. However, this material decomposed due to the heat generated by the microwave discharge. It was found necessary thereafter to use a thin-walled glass tube. The traps in both the reaction line and the fractionating train were constructed of monel, while the line was made of copper tubing.

Micrometer valves were used to gain the high degree of control over reactant flow rates. Large bore, blunt-end valves were used in the reaction line to insure unrestricted flow through the discharge tube. The source of microwave energy was a Raytheon microtherm unit, Model KV-104A, with a maximum power of 100 watts at 2450 ± 25 megacycles.

Procedure

The system was evacuated and the microwave discharge was started. It was necessary to initiate the discharge with a Tesla coil. From then on it was maintained with the microwave radiation. The discharge tube was cooled by passing ambient temperature air over it. The reactants were metered into the reaction tube through calibrated flow meters.

In some experiments, both reactants were passed through the discharge zone. In others, when it was thought that one of the reactants did not need activation, this reactant was added immediately after the discharge zone. The products were then condensed in -196°C. traps and the gases, non-condensible at -196°C., were pumped off. Infrared and mass spectrometric analyses were used to identify the products.

Figure 34

Microwave Discharge Apparatus
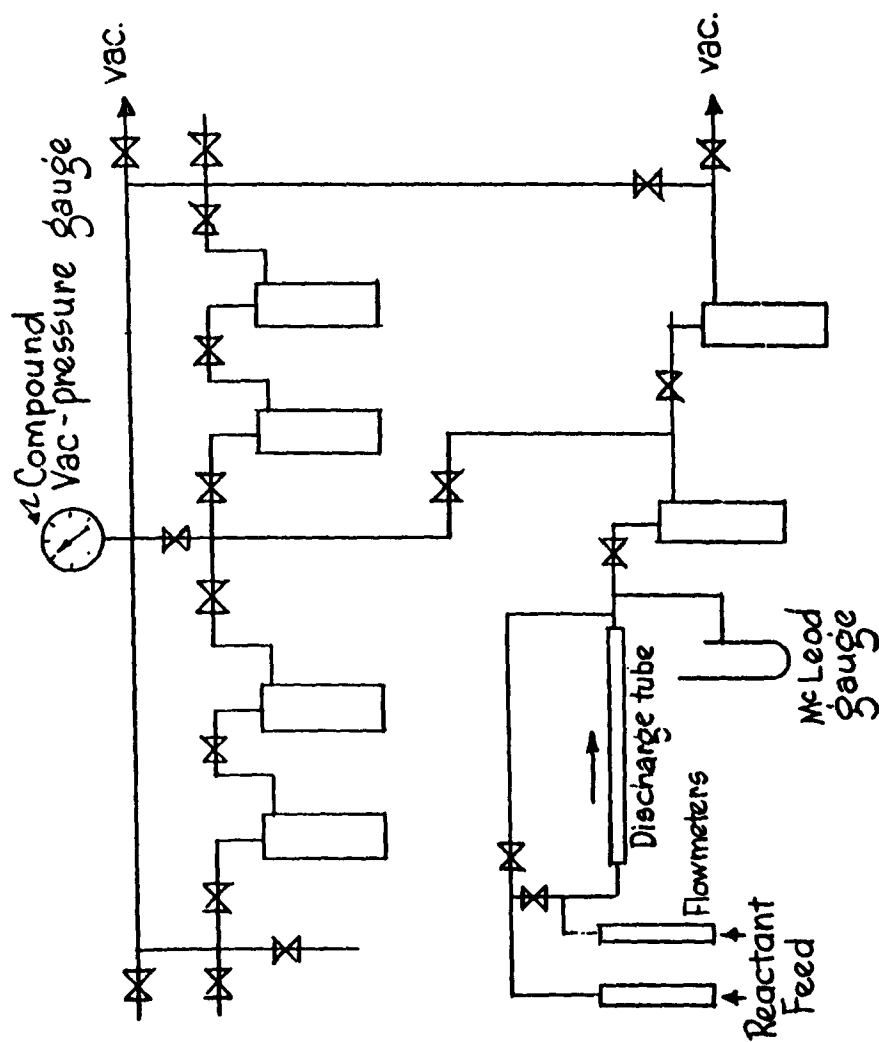
Results

The results of this experiment are summarized in Table 58, Experiment 1810D-63.

Under mild conditions perchloryl fluoride does not react with tetrafluorohydrazine (107,108) and microwave activation was selected to provide the supposed energy requirements for the following reaction,

$$FClO_3 + NF_2\text{-}NF_2 \longrightarrow NF_2ClO_3 + NF_3$$
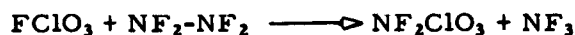
When perchloryl fluoride and tetrafluorohydrazine were passed through the microwave reaction tube, all of the tetrafluorohydrazine was decomposed but most of the perchloryl fluoride was recovered. Some nitrogen oxides were formed either by reaction of N_2F_4 with a portion of the perchloryl fluoride or, more probably, reaction with small amounts of air that leaked into the system since the discharge tube is operated under reduced pressure. There was no evidence for the presence or formation of NF_3 or the desired product NF_2ClO_3.

Pure tetrafluorohydrazine alone was passed through the microwave discharge to determine whether the activation generated NF_2 radicals or decomposition of N_2F_4 to the elements N_2 and F_2 occurred.

If the N·N bonds in N_2F_4 were broken and NF_2 radicals formed, some recombination undoubtedly would occur but N_2F_4 should be recovered. Only a small amount of tetrafluorohydrazine was recovered. A large amount of volatile gases, not condensible at -196°C., formed.

Since microwave activation appeared to be too energetic for reactions involving N_2F_4, the reaction of N_2F_4 with perchloryl fluoride in fluorosulfonic acid was investigated in an attempt to prepare difluoroamine chlorate:

$$N_2F_4 + FClO_3 \xrightarrow{\text{HSO}_3\text{F}} NF_2ClO_3 + NF_3$$

At 25°C. there was no evidence of a reaction. The results of this experiment are summarized in Table 59, Experiment 1810D-89.

The reaction of perchloryl fluoride with tetrafluorohydrazine was also investigated in the electric discharge apparatus described in Figure 35. When both reactants were passed through the discharge tube extensive decomposition of the tetrafluorohydrazine occurred but most of the perchloryl fluoride was recovered. Some interaction of the Pyrex discharge tube walls occurred with either tetrafluorohydrazine or with the decomposition products of tetrafluorohydrazine, as evidenced by the presence of SiF_4 in the products. There was no evidence for the presence of NF_2ClO_3 in the products. The results are summarized in Table 60, Experiment 1810D-46.

(c) FClO₃ + NF₃

Material

FClO₃.   Pennsalt Chemical Co., purity 99.9%

NF₃.   Peninsular Chemical Research Corp.

Table 58

Microwave Discharge Reactions

Experiment Number	Reaction Time (hours)	Power Output (watts)	Flow Rates of Reactants (ml/min)	Weight of Solid Reactant (g.)	Weight Loss of Solid (g.)	Discharge Tube Used	Product Analysis	Comments
1810D-62	0.5	95-100	$\frac{NF_3}{12}$ $\frac{Cl_2}{12}$	-	-	Teflon 1/4"	Trace of N_2F_4, N_2O, Cl_2, CF_4 and CF_3Cl	Teflon tube decomposed in the heat generated by discharge
1810D-63	0.75	100	$\frac{NF_3}{10}$ $\frac{FClO_3}{10}$	-	-	5 mm glass tube	Nitrogen oxides. $FClO_3$	All of the N_2F_4 destroyed; no solids were found.
1810D-64	1.5	100	$\frac{NF_3}{15}$ $\frac{FClO_3}{15}$	-	-	Thin walled glass tube 3 mm. D.	$FClO_2$, NF_3, some nitrogen oxides	Most of the NF_3 and $FClO_3$ recovered.
1910D-65	1.0	100	$\frac{NF_3}{12}$	$\frac{KClO_4}{0.2065}$	0.0215	Thin walled glass	No solid or condensable products found	N_2F_4 decomposed to elements- $KClO_4$ lost oxygen
1810D-67	1.5	100	$\frac{NF_3}{15}$	$\frac{KClO_4}{0.6986}$	0.1210	Thin walled glass tube	Trace of NF_3	$KClO_4$ lost oxygen all N_2F_4 decomposed
1810D-68	1.75	100	$\frac{NF_3}{20}$	$\frac{LiClO_4}{0.6792}$	0.1265	Thin walled glass tube	Nitrogen oxides. Trace of NF_3.	The NF_3 was found to be an impurity in N_2F_4
1810D-70	1.5	100	$\frac{NF_3}{26}$	$\frac{LiClO_4}{0.6182}$	0.0331	Thin walled glass tube	Nitrogen oxides.	$LiClO_3$ lost oxygen
1810D-72	2.0	100	$\frac{NF_3H}{15}$ $\frac{He}{15}$	$\frac{LiClO_4}{0.8135}$	-	Thin walled glass tube	No reaction.	
1810D-73	1.0	90	$\frac{HClO_4}{15}$ $\frac{N_2F_4}{20}$	-	-	Thin walled glass tube	Nitrogen oxide. N_2F_4	The N_2F_4 was added after discharge - all $HClO_4$ decomposed

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Table 59

General Reactions of Tetrafluorohydrazine

Expt. No.	Reaction Time hrs.	Temp of Reaction °C	Weight of Reactants g.	Analysis of Products Solid	Volatile	Comments
1810D-85	2.0	25	$KClO_3$ 2.735 / N_2F_4 0.81	34.3%K, 21.1%Cl, 2.4%N, 4.1%F	ClO_3F, N_2O, NO_2, NF_3, N_2F_4	Much more ClO_3F than in previous experiments. The SiF_4 was probably formed in the infra red cell.
1810D-86	20.0	25	$KClO_3$ 3.219 / N_2F_4 1.67	42.3%K, 18.4%Cl, 2.2%N, 8.7%F	ClO_3F, NF_3, N_2O, NO_2, SiF_4	
1810D-87	5.0	25	KNO_3 2.635 / N_2F_4 1.43	41.1%K, 13.3%N, 1.5%F	NF_3, N_2F_4, NO_2	The materials reacted only slightly.
1810D-89	48	-78 to 25	ClO_3F 2.2 / N_2F_4 1.7	10 ml. of HSO_3F	N_2F_4, ClO_3F	The ClO_3F is slightly soluble in HSO_3F. No reaction occurred.

Table 60

Electric Discharge Reaction

Experiment Number	Length of Expt. (hrs.)	Potential Drop (volts)	Flow Rate of Reactants (ml./min.)		System Pressure (mm. of Hg)	Analysis of Solid Products	Analysis of Volatile Products	Comments
1810D-38	0.5	15,000	NF_3 (a) 35	$HClO_4$ (b) 35	0.8	8.93% N No F	Not analysed	Perchlorate ion was not identified in the products.
1810D-39	0.75	5,000	NF_3 (a) 35	$HClO_4$ (b) 35	1.0	-	SiF_4, N_2O, NO_2, chlorine oxides, ClO_2F	Solid products were decomposed by reaction with moisture.
1810D-41	0.75	4,000	NF_3 (a) 35	$HClO_4$ (b) 35	1.1	7.9% N 18.7% Cl No F	Not analysed	Solids appear to be NO_2ClO_4
1810D-42	1.0	4,000	NF_3 (a) 40	$HClO_4$ (b) 35	1.2	Not analysed	I. R. showed N-F bands, also some bands present in ClO_2F absorption region	Volatile products reacted with water. Soln. gave strong KI Test.
1810D-43	1.25	4,000	NF_3 (a) 40	$HClO_4$ (b) 35	1.2	Not analysed	Volatile products from -196° trap were hydrolysed in strong KOH. The gases evolved and the KOH soln. were then analysed. Gas (1.7 g.) 90% NF_3 Soln. 36.3% F, 29% Cl⁻, 14.4% Cl as perchlorate	
1810D-45	0.25	2,300	N_2F_4 (a) 25	$HClO_4$ (b) 35	0.9	•	SiF_4, N_2O, NO_2, No N_2F_4	♦ Only small amount of solids formed. Evolved NO_2 on hydrolysis, appeared to be NO_2ClO_4.
1810D-46	0.25	3,500	N_2F_4 (a) 25	ClO_2F (a) 40	1.1	No solid products formed	SiF_4, N_2O, ClO_2F, Cl_2	There was a large band at 11 microns in the I. R. spectrum which was not identified.
1810D-48	0.75	4,300	NF_3 (a) 30	ClO_2F (a) 40	1.4	No solid products formed	NH_3, ClO_2F, Cl_2	
1810D-50	1.25	4,100	NF_3 (a) 35	$HClO_4$ (b) 35	1.1	9.7% N 23.5% Cl	NF_3, ClO_2F, SiF_4, N_2O, possibly some NO_2F	Solid product appears to be NO_2ClO_4.
1810D-52	0.1	1,600 (20 milli amps)	N_2F_4 (a) 15	Cl_2 (a) 35	0.7	No solids formed	Cl_2, SiF_4, NO_2, possibly NO_2F	Attempted preparation of NF_2Cl.
1810D-53	0.75	2,600 to 3,100	NF_3 (a) 30	Cl_2 (a) 30	0.8 to 1.0	No solids formed	Cl_2, NF_3, NO_2, SiF_4	Several unidentified bands in I. R. spectra.

(a) Reactant was passed through discharge.
(b) Reactant admitted after discharge.

Apparatus

This reaction was conducted in the microwave discharge apparatus described in Figure 34 and the electric discharge apparatus described in Figure 35. The microwave reaction tube was constructed of thin-walled Pyrex glass. The traps in both the reaction line and the product fractionating train were constructed of monel, while the converting lines were constructed of copper tubing. Micrometer valves were used to gain the high degree of control over reactant flow rates. Large bore, blunt-end valves were used in the reaction line to insure unrestricted flow through the discharge tube. The source of microwave energy was a Raytheon Microtherm Unit, Model KV-104A, with a maximum power of 100 watts at 2450 ± 25 megacycles.

The electric discharge apparatus, Figure 35, consisted of a modified Woods tube which was constructed of Pyrex glass. Two copper plates served as electrodes.

Procedure

For reactions utilizing microwave activation, the following procedure was used. The system was evacuated and the microwave discharge was started with a Tesla coil. The gaseous reactants were metered into the reaction through calibrated fluorometers. The products were collected in traps cooled to -196°C.

In reactions utilizing electric discharge activation, the discharge tube was evacuated and low temperature baths were placed around the product traps. Dry ice was then packed around the discharge tube to provide cooling for the discharge tube. The gaseous reactants were metered through differential pressure capillary flow meters into the discharge tube. The products were collected in the low temperature traps, fractionated, and analyzed.

Results

The results of the experiment with microwave activation are summarized in Table 58, Experiment 1810D-64.

Since both NF_3 and $FClO_3$ are very stable compounds which do not react readily, it was reasoned that some vigorous activation was needed to promote the following proposed reactions,

$$NF_3 + FClO_3 \longrightarrow NF_4ClO_3$$

or

$$NF_3 + FClO_3 \longrightarrow NF_2ClO_3 + F_2$$
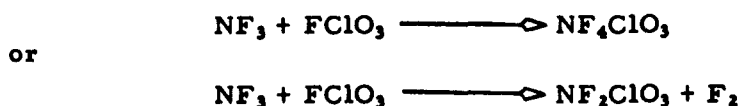
When a gaseous mixture consisting of $FClO_3$ and NF_3 was passed through the microwave discharge tube, both reactants were recovered in the product traps. Trace amounts of nitrogen oxides were also detected in the products but this could be due to trace impurities in the nitrogen trifluoride. Essentially, there was no reaction between NF_3 and $FClO_3$ when these reactants were subjected to microwave excitation.

Figure 35

Electric Discharge Apparatus

Reactants

Copper Electrode

Copper Electrode

McLeod Gauge

Vacuum

15,000 Volt Transformer

110 V. A.C.

R₁

R₂

Ⓐ - Amp. meter   0-100 milliamps

Ⓥ - Voltmeter   0-5000 volts

R₁ - Power stat

R₂ - 0-100,000 ohm   Variable resistor

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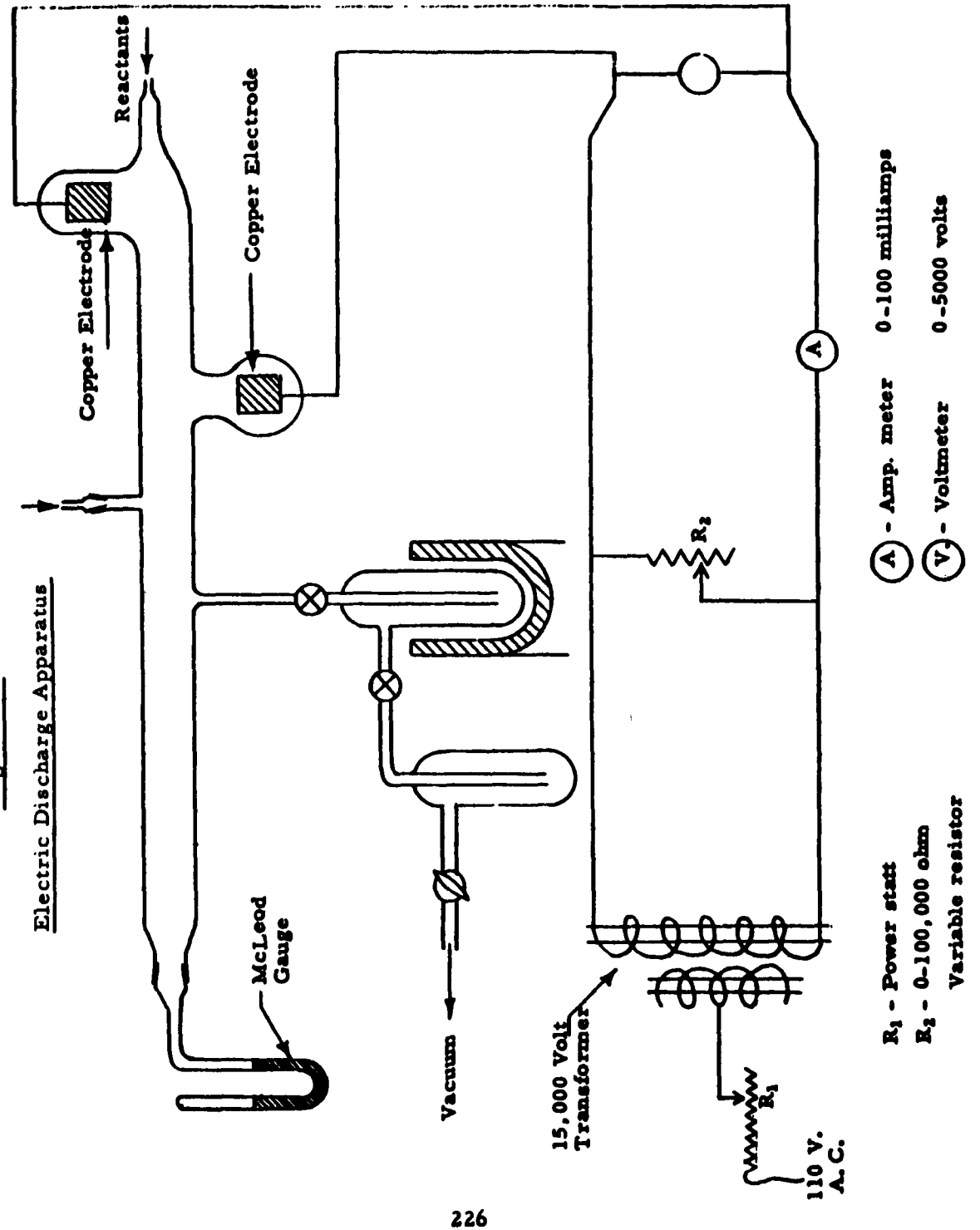
The results of an experiment employing silent electric discharge activation are summarized in Table 60, Experiment 1810D-48. In this case, also, both reactants were recovered. There was no evidence of a reaction.

C. Reactions with $FClO_2$

1. Objective

The primary objective of this program was to prepare light weight metal oxyfluorochlorate salts by solvolysis of metal fluorides in chloryl fluoride according to the general equation,

$$M^+F^- + FClO_2 \longrightarrow M^+(ClO_2F_2)^-$$

where

$$M = NO^+, Li^+, Cs^+, Mg^{++}, or NH_4^+$$
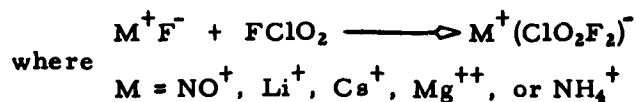
This study was, in part, prompted by the reported synthesis of a new series of compounds by Mitra and Ray (56) which contained an oxy-fluoro anion of chlorine; $ClO_3F^=$. (See Section IX).

If compounds containing such anions could be prepared, it was reasoned that the alkali metal fluorides might react as bases with chloryl fluoride to form a new series of compounds,

$$Li^+F^- + FClO_2 \longrightarrow Li^+ClO_2F_2^-$$

(a) $FClO_2 + NOF$

Material

$FClO_2$. Chloryl fluoride was prepared by the method of Schmeisser and Fink (55) by the following reactions:

$$Cl_2 + NaClO_2 \longrightarrow ClO_2 + NaCl$$

$$ClO_2 + AgF_2 \longrightarrow FClO_2 + AgF$$

The $FClO_2$, a colorless or sometimes pale yellow liquid, was identified by infrared.

NOF. Nitrosyl fluoride was prepared by the method of Brauer (13) by the reaction of fluorine with nitrogen oxide in the apparatus described in Figure 5.

$$2NO + F_2 \longrightarrow 2NOF$$

Apparatus

The apparatus consisted of a Kel-F reactor described in Figure 36 which was attached to a general purpose metal high vacuum transfer line.

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Procedure

Weighed quantities of nitrosyl fluoride and chloryl fluoride were vacuum distilled into the Kel-F reactor which was cooled to -196°C. The steel top of the reactor was coated with Kel-F grease before assembly to minimize the possibility of a reaction taking place with the stainless steel cap and the reactants. The reactor was then closed, the reactants warmed to 25°C. and held there for two hours with continuous agitation. The reactor was then cooled to -78°C. and the product fractions at -78°, -46°, -23°, 0°, and 25°C. were collected and analyzed.

Results

The objective of this work was to determine whether chloryl fluoride would react as an acid with nitrosyl fluoride to form a new oxyfluoro-chlorate salt:

$$NOF + FClO_2 \longrightarrow NO^+ClO_2F_2^-$$

This reaction would be somewhat analogous to the observed reaction of nitrosyl fluoride and chlorine trifluoride described in IA, 5a.

$$NOF + ClF_3 \longrightarrow NO^+ClF_4^-$$

At 25°C. there was no evidence of a reaction between nitrosyl fluoride and chloryl fluoride. The reactants were recovered.

b. $FClO_2 + LiF$

Material

$FClO_2$. Prepared as previously described.

LiF. American Potash and Chemical Corporation

Apparatus

The apparatus consisted of a reactor constructed of Kel-F and stainless steel as described in Figure 36 which was attached to a general purpose metal high vacuum line.

Procedure

The lithium fluoride was placed in the reactor, the reactor closed, and connected to the vacuum transfer line. The reactor was cooled to -196°C. and 3 milliliters of $FClO_2$ was distilled into the reactor. The reactor was then closed, and the reactants held 26°C. for two hours. The products were fractionated and analyzed.

Results

The objective of this experiment was to promote the formation of a light weight metal oxyfluorochlorate salt by solvolysis of lithium fluoride in chloryl fluoride:

$$LiF + FClO_2 \longrightarrow Li^+ClO_2F_2^-$$

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NH-2090

Figure 36

Kel-F and Stainless Steel Reactor
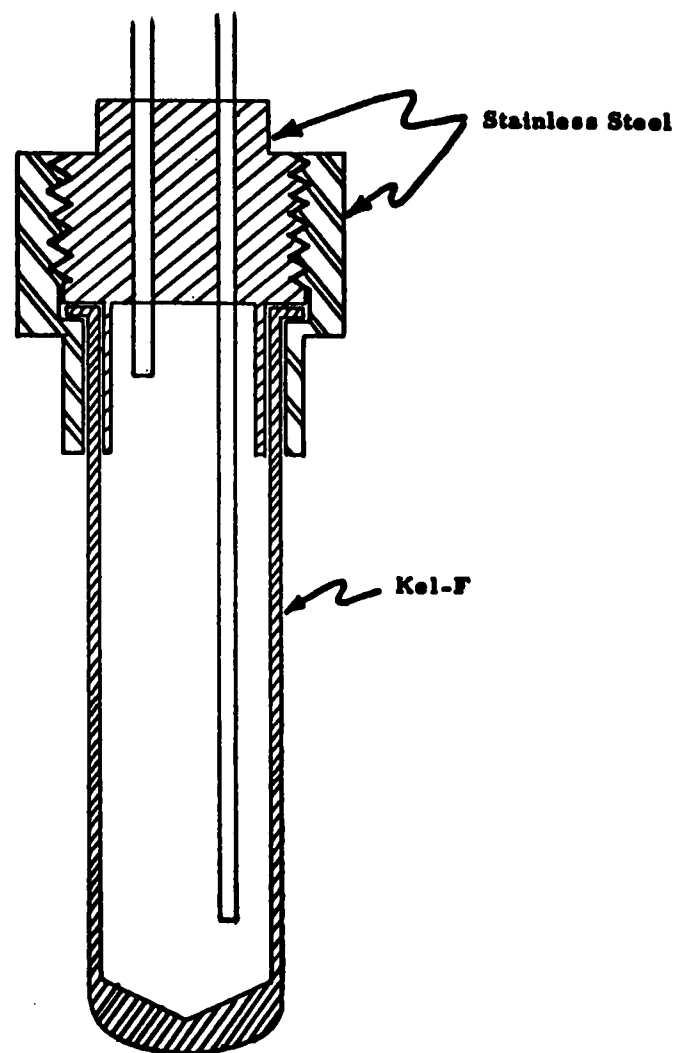
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The results of these experiments are summarized in Table 61, Experiments 1859D-15 and 1859D-17.

The solid material was removed from the reactor at the completion of one experiment and analyzed.

		Found	Theoretical for $LiClO_2F_3$	LiF
Wt. %	F	61.4	33.8	73.2
	Cl	1.4	31.5	-
	Li	22.5	6.2	26.8
	O	—	28.5	-
			100.0	100.0

The analysis indicated that the recovered solid consisted mostly of unreacted lithium fluoride. There was no evidence of a reaction other than partial decomposition of the chloryl fluoride.

c. $FClO_2$ + CsF

Material

$FClO_2$. Prepared as described.

CsF. American Potash and Chemical Company

Apparatus

The apparatus consisted of the Kel-F reactor described in Figure 36 which was attached to a general purpose metal high vacuum transfer line.

Procedure

In a nitrogen dry box, 2.78 g. of CsF was placed in the reactor. The reactor was then attached to the transfer line , evacuated, cooled to -196°C. and 4 milliliters of chloryl fluoride condensed in. The reactants were held for two hours at 20°C. The product was then fractionated and analyzed.

Results

The results are summarized in Table 61, Experiment 1859D-22.

The objective of this study was to determine whether the solvolysis of cesium fluoride in chloryl fluoride would produce a salt which contained an oxyfluoro anion, but there was no evidence of a reaction. The cesium fluoride was recovered.

$$CsF + FClO_2 \longrightarrow Cs^+ClO_2F_2^-$$

Table 61

Reactions with Chloryl Fluoride

Experiment Number	Temperature of Reaction °C	Volume or Weight of Reactants g	ml	Weight of Solid Product Recovered g	Analysis and Remarks
1859D - 15	-196 to 26	LiF 2.09	ClO₂F 3	2.28	% Li = 22.5 %F = 61.9% %Cl = 1.4% % ClO₂ = 0.00%
1859D - 17	-78 to 75	LiF 2.66	ClO₂F 3	2.67	No analysis obtained - solid appearance unchanged and only negligible weight change.
1859D - 22	-78 to 20	CsF 2.78	ClO₂F 4	2.30	No evidence of reaction - No change in appearance of the solids.

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d. $FClO_2$ + MgF_2

Material

$FClO_2$. Prepared as described.

MgF_2. Allied Chemical and Dye Corporation.

Apparatus

The apparatus consisted of the Kel-F reactor described in Figure 36.

Procedure

The reactor was charged with approximately 2 grams of magnesium fluoride in a nitrogen dry box. The reactor was then attached to the transfer line, and approximately 4 milliliters of perchloryl fluoride condensed into the reactor. The reactor was closed and the reactants were held at 25°C. for two hours. The product was then fractionated and analyzed.

Results

The objective of this experiment was to determine whether the solvolysis of magnesium fluoride in chloryl fluoride would result in the formation of a salt containing an oxyfluoro anion, i.e.:

$$MgF_2 + 2FClO_2 \longrightarrow Mg^{++}(ClO_2F_2)_2$$

There was no evidence of a reaction. The magnesium fluoride was recovered.

Section VI Reactions with N-F Intermediates

    A. Reactions with N_2F_4

        1. Objective

Most of the reactions selected for investigation with N_2F_4 were based on the premise that NF_2 radicals are energetic species and that these radicals would undergo chemical reactions with various metal salts in a manner analogous to fluorine or chlorine (52):

$$F_2 + KClO_3 \longrightarrow KF + FClO_3$$

$$Cl_2 + NaClO_2 \longrightarrow NaCl + ClO_2 + 1/2\ Cl_2$$

$$N_2F_4 + KClO_3 \longrightarrow KNF_2 + NF_2ClO_3$$

$$N_2F_4 + NaClO_2 \longrightarrow NaNF_2 + NF_2ClO_2$$
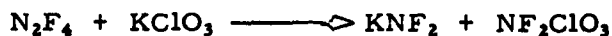
Englebrecht and Atzwanger (52) observed that when fluorine gas reacts with solid potassium chlorate, the by-products of this reaction are Cl_2, ClO_2F, O_2, Cl_2O_6 and ClF all of which could be explained by a free radical mechanism involving fluorine and a chlorate radical.

Since tetrafluorohydrazine dissociates readily to NF_2 radicals (66)

$$N_2F_4 \rightleftharpoons 2NF_2$$

it was proposed that N_2F_4, with appropriate activation such as ultraviolet, microwave, or thermal, would react with various metal salts to form a series of new highly energetic oxidizers, such as:

$$N_2F_4 + KClO_4 \longrightarrow NF_2ClO_4 + KF + N_2F_2$$

$$N_2F_4 + KNO_3 \longrightarrow NF_2NO_3 + KF + N_2F_2$$

$$N_2F_4 + NaClO_2 \longrightarrow NF_2ClO_2 + NaF + N_2F_2$$

        a. $N_2F_4 + KClO_4$

Material

    N_2F_4. E. I. DuPont de Nemours and Company, purity 99%.

    $KClO_4$. Fisher Scientific Company, purity 99.9%.

Apparatus

The apparatus is described in Figure 12. Side reactions of N_2F_4 with glass were eliminated by using only Teflon for the reactor, and polypropylene, copper, and stainless steel in the construction of the system. A Hanovia No. 30600 ultraviolet lamp (1849-4000 Å) light source was employed.

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Procedure

In a typical experiment, potassium perchorate, previously dried at 100°C. for two hours, was placed in the reactor cavity, and the reactor system sealed and evacuated. Approximately 0.6-0.8 g. of solid was generally employed. The distance from the lamp to the cell body was approximately 2-3 inches. The reactor system was generally flushed several times with dry nitrogen, evacuated, and a weighed quantity of N_2F_4 was admitted to a pressure of about 400 mm. The recycle trap was cooled with Dry Ice, the bellows pump turned on and the sample irradiated for a period of 3-4 hours. The gaseous products then were collected in a trap (-196°C.) and the solid and gaseous materials weighed and analyzed.

Results

A novel approach for the synthesis of NF_2ClO_4 is the reaction between photoactivated N_2F_4 and potassium perchlorate. The postulated reaction is:

$$N_2F_4 \xrightarrow{U V} 2NF_2 \xrightarrow{U V} 2NF\cdot + 2F\cdot$$

$$F + KClO_4 \longrightarrow KF + ClO_4$$

$$NF + KClO_4 \longrightarrow KF + 1/2N_2 + ClO_4$$

$$NF_2 + ClO_4 \longrightarrow NF_2ClO_4$$
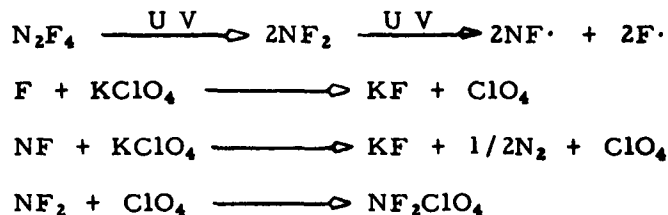
The results of these experiments are summarized in Tables 62 and 63.

The initial experiments were conducted to determine the effectiveness of the reactor system and three experiments were conducted to test the inertness of the reactor toward N_2F_4. In each of the experiments the N_2F_4 was collected unchanged after circulating for three hours.

A series of experiments also was conducted to investigate the effect of the irradiation of N_2F_4 itself. When unfiltered light (1849-4000 Å) from the Hanovia lamp is used, the expected decomposition of the N_2F_4 occurs to give NF_3 and a gas, noncondensable at -196°C., presumed to be nitrogen.

$$3N_2F_4 \xrightarrow[1849-4000Å]{U. V.} 4NF_3 + N_2$$
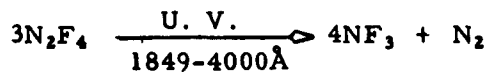
Based on infrared analyses, it is estimated that a 50-70 per cent conversion of the N_2F_4 occurs over a period of 3-4 hours.

When Vycor and NiO_2 filters were used to allow transmission of irradiation from 2500-3700 Å, the N_2F_4 was recovered unchanged and products such as NF_3, N_2F_2, and N_2 could not be detected. With the Vycor filter alone, 2100-4000 Å transmission, it was again shown that no decomposition of the N_2F_4 occurred. These results are in conflict with the work of Rohm and Haas (57) who irradiated N_2F_4 at 2500 Å and found complete conversion to NF_3 and N_2F_2 over a 15-minute period. This work was done with

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Table 62

Ultraviolet Irradiation of N_2F_4

Experiment No.	1602-84A	1602-84B	1602-85A	1602-85B	1602-86A	1602-87A
N_2F_4	390 mm.	365 mm.	240 mm.	375 mm.	350 mm. 0.1830 g.	350 mm. 0.1870 g.
Temperature	R. T.	R. T.	R. T.	R. T.	R. T.	R. T.
Irradiation Period	3 hr.	3 hr.	3 hr.	2 hr.	4 hr.	4 hr.
Irradiation Band	1849-4000Å	1849-4000Å	2500-3700Å	2500-3700Å	2100-4000Å	1849-4000Å
Product Analysis	~50% Conversion to NF_3 and N_2	~70% Conversion to NF_3 and N_2	0% Conversion, only N_2F_4	0% Conversion, only N_2F_4	0% Conversion, only N_2F_4*	~50% Conversion to NF_3 and N_2

* No Reaction With $KClO_4$ Present

Hanovia No. 30600
U. V. Lamp
Vycor Filter
NiO_2 Filter

1849Å   2100Å   2500Å   3700Å   4000Å   4000Å

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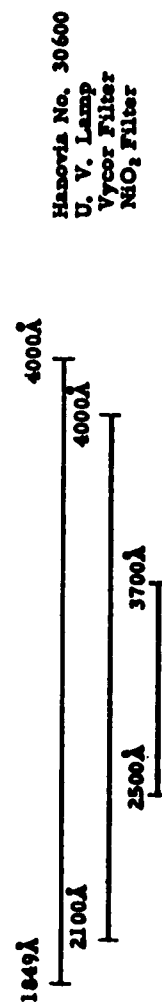
Table 63

Reaction of Irradiated N_2F_4 with $KClO_4$

Experiment No.	1602-91	1602-93	1602-94	1602-96
N_2F_4 (g.)	0.4810	0.5590	0.7880	0.9170
$KClO_4$ (g.)	0.5419	0.7702	0.7739	0.6994
Temperature (N_2F_4)	100°C	R.T.	100°C	100°C
Reaction Time (Hr.)	3.5	4	4	4
I.R. Analysis (Solid) (Nujol Mull)	$KClO_4$ plus Band at 10.3	$KClO_4$ only	$KClO_4$ plus bands for Kel-F grease at 7.9, 8.4 8.9, 10.3 and 11.2	$KClO_4$ only
I.R. Analysis (Gases)	N_2F_4, NF_3 plus trace of NO_2 and NOF	N_2F_4, NF_3 plus trace of N_2O NO_2 and NOF	N_2F_4, NF_3 plus trace of N_2O, NO_2 and NOF	N_2F_4, NF_3 plus trace of N_2O, NO_2 and NOF
X-ray analysis (solid)	$KClO_4$ only	-	-	-

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a Kharasch-Friedlander lamp in a glass reactor (SiF_4 was found to be one of the products) and it appears that the glass may have acted as a catalyst for the decomposition of N_2F_4 at wavelengths where significant absorption of radiation by the N_2F_4 does not occur.

In experiment 1602-86A, Table 62, the Vycor filter (2100-4000$\overset{\bullet}{A}$) was used and all of the N_2F_4 was recovered. In experiment 1602-87A, Table 62, the filter was removed and decomposition of N_2F_4 occurred, but there was no reaction with the $KClO_4$.

The more significant experiments of a large number are summarized in Table 63. Infrared and X-ray examination of the $KClO_4$ showed that it was unaffected and only trace amounts of N_2O, NO_2 and NO were detected. Apparently $KClO_4$ is immune to the action of fluorine atoms

$$F\cdot \ + \ KClO_4 \ \xrightarrow{\quad\diagup\quad} ClO_4\cdot \ + \ KF$$

or the irradiation of N_2F_4 with ultraviolet light does not produce fluorine radicals.

$$NF_2 \ \xrightarrow{\ U.V.\ } F\cdot \ + \ NF\cdot$$

In the presence of glass traps in the system, the reaction of U.V. irradiated N_2F_4 with $KClO_4$ results in the formation of $(NO_2)_2SiF_6$ and SiF_4 plus gaseous decomposition products including NF_3, NO_2, N_2O and NOF. Infrared examination of the $KClO_4$ showed the presence in the spectrum, on occasions, of absorption peaks in the N-O region which resembled those for NO_2 and NO_3^-. Elemental analysis of the $KClO_4$ revealed the absence of both nitrogen and fluorine. Chlorine values obtained agreed closely with those calculated for $KClO_4$.

The effect of glass and quartz on the U.V. irradiated N_2F_4 was investigated by passing N_2F_4 alone through the system. In the presence of trace amounts of water vapor a reaction did occur leading to the decomposition products NF_3, NO_2, N_2O and NOF. Etching of both the glass and quartz occurred and $(NO_2)_2SiF_6$ was deposited.

Under anhydrous conditions with the glass traps replaced by ones constructed of polypropylene and Teflon, little reaction occurred. The U.V. activated N_2F_4 was recovered almost intact with only a trace of NF_3, NOF, and N_2O appearing. The absence of SiF_4 in the gaseous products was very significant.

The reaction of N_2F_4 with $KClO_4$ was also investigated in the apparatus described in Figure 34. In this system solid $KClO_4$ was placed in a thin-walled Pyrex tube and a gas stream of N_2F_4 was passed over the solid while the reactants were activated with microwave energy supplied by a Raytheon microtherm unit, Model KV-104A, with a maximum power of 100 watts $\pm$ 25 megacycles.

The results of this work are summarized in Table 58, Experiment

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1810D-67. All of the N_2F_4 and some of the $KClO_4$ decomposed, but there was no evidence for the formation of the desired product NF_2ClO_4. Microwave activation of N_2F_4 alone caused complete decomposition and this activation probably would have decomposed any NF_2ClO_4 formed.

b. N_2F_4 + $LiClO_4$

Materials

N_2F_4. Prepared as described in Section X; purity 99%.

$LiClO_4$. American Potash and Chemical Corporation

Apparatus

The microwave discharge apparatus is described in Figure 34. The reactor consisted of a thin walled Pyrex tube. Product traps were constructed of monel, while the connecting lines were made of 1/4" O.D. copper tubing. Micrometer valves were used to provide a high degree of gas flow control. Large bore, blunt end valves were used in the reaction line to insure unrestricted flow through the discharge tube. The source of microwave energy was a Raytheon microtherm unit, Model KV-104A, with a maximum power of 100 watts at 2450 ± 25 megacycles.

Procedure

Solid $LiClO_4$ (0.6g.) was placed in the reactor and the tube evacuated. The microwave generator was started and a slow stream of N_2F_4 was passed through the discharge tube. The volatile products were collected in a series of traps cooled to -196°C. The discharge tube was cooled by passing air over the tube to prevent possible decomposition of solid products that might form and remain in the tube. The products were then fractionated and analyzed.

Results

The results of one experiment are summarized in Table 58, Experiment 1810D-68.

This experiment was conducted to determine whether microwave activation of N_2F_4 and $LiClO_4$ would produce a reaction as follows

$$N_2F_4 \longrightarrow 2NF_2 \cdot \longrightarrow 2NF \cdot + 2F$$

$$F \cdot + LiClO_4 \longrightarrow LiF + ClO_4 \cdot$$

$$NF_2 \cdot + ClO_4 \cdot \longrightarrow NF_2ClO_4 \cdot$$

$$2NF \cdot \longrightarrow N_2F_2$$
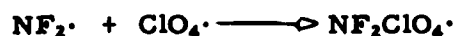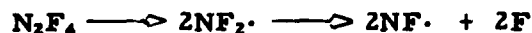
All of the N_2F_4 was decomposed to nitrogen oxides, and probably fluorine and nitrogen. Traces of NF_3 were also detected in the gaseous

decomposition products but this NF_3 may have originated as an impurity in the N_2F_4. The recovered $LiClO_4$ had decomposed slightly: 0.1265g. less than the 0.6792g. added, but there was no evidence of a reaction or the presence of NF_2ClO_4 in the products.

It was concluded that no significant reaction occurred between $LiClO_4$ and N_2F_4 or the decomposition products of N_2F_4.

c. N_2F_4 + $LiClO_3$

Material

N_2F_4. Prepared as described in Section X; purity 99%.

$LiClO_3$. American Potash and Chemical Corporation

Apparatus

The apparatus is described in Figure 37. The reactor consisted of a Vycor vessel, approximately 100-ml. volume, which was connected to a high vacuum line constructed of copper tubing and a Monel product trap.

Procedure

In a typical experiment 1-2 grams of $LiClO_3$ was placed in the Vycor reactor and the reactor and high vacuum transfer line were evacuated. The reactor was then pressured with N_2F_4 to atmospheric pressure and the reactants were held for 1-2 hours at 25°C while the solid $LiClO_3$ was stirred with a magnetic Teflon coated stirring bar. The products were then fractionated and analyzed.

Results

The results of three experiments are summarized in Table 64.

Since N_2F_4 can be considered as a psuedo-halogen, it was postulated that the following reaction might occur:

$$N_2F_4 + LiClO_3 \longrightarrow NF_2ClO_3 + LiNF_2$$

$$2\,LiNF_2 \longrightarrow 2\,LiF + N_2F_2$$
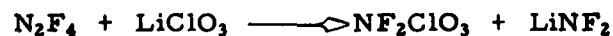
When tetrafluorohydrazine was added to the Vycor reactor which contained $LiClO_3$, an immediate reaction occurred, the system was immediately filled with brown gas and the reactor became quite warm. The gaseous products consisted of nitrogen oxides, $FClO_3$, SiF_4 and NF_3. Analysis of the solid product recovered from the Vycor reactor did not

Figure 37

Apparatus for Reactions of Tetrafluorohydrazine

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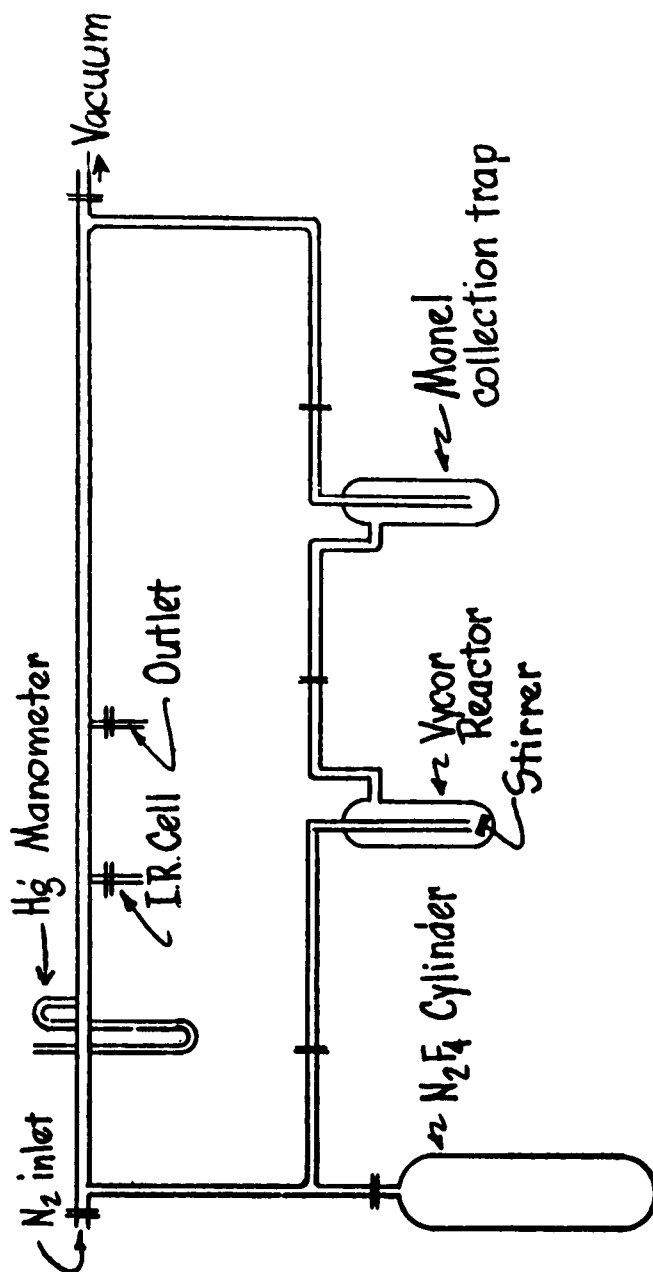
Table 64

Reaction of Tetrafluorohydrazine and Lithium Chlorate

Exp. No.	Weight of Li ClO₄ g.	Weight N₂F₄ g.	Temp °C	Time hrs.	RESULTS Elemental analysis of solids				Infared analysis of gases
					Li %	Cl %	F %	N %	
1928D-43		0.9	25	1	8.4	16.5	7.95	7.70	N_2O, NO_2, NF_3, SiF_4, Trace $FClO_3$
1928D-48	2.16	0.9	25	2	8.5	30.0	6.04	3.35	N_2O, NO_2, NF_3, SiF_4, $FClO_3$
1928D-64	2.07	2.52	-160	1	8.3	36.3	1.03	0.45	N_2O, NO_2, NF_3, [a]

[a] A monel reactor was substituted for the vycor reactor

support the presence of NF_2ClO_3

	Found			Theoretical For
	#43	#48	#64	NF_2ClO_3
Wt. % F	7.9	6.0	1.0	28.1
Cl	16.5	30.0	36.3	26.2
N	7.7	3.4	0.5	10.3
Li	8.4	8.5	8.3	-
O	-	-	-	35.4
				100.0

The solid product was probably a mixture of LiF and $LiClO_3$.

When this experiment was repeated using very dry $LiClO_3$ (dried 20 hours at 120°C), there was no evidence of a reaction in the Teflon reactor.

It was concluded that decomposition of N_2F_4 occurred in the initial experiment due to the presence of moisture in the $LiClO_3$ and the possible catalytic effect of Vycor.

The reaction of $LiClO_3$ with N_2F_4 was also investigated in a thin walled glass tube using microwave discharge activation. The apparatus is described in Figure 34. The microwave activation was supplied by a Raytheon Microtherm Unit, Model KV-104A, with a maximum power of 100 watts at 2450 $\pm$ 25 megacycles.

The results are summarized in Table 58, Experiment 1810D-70.

A slight reaction or simple decomposition of the $LiClO_3$ occurred. All of the N_2F_4 was decomposed to nitrogen oxides, and probably fluorine and nitrogen. The recovered $LiClO_3$ had lost weight (about 5%), but this loss could have been due to reaction of impurities or absorbed water with the tetrafluorohydrazine. There was no evidence for the formation of the desired product NF_2ClO_3.

d. N_2F_4 + $KClO_3$

Material

N_2F_4. Prepared as described in Section X.

$KClO_3$. Mallinskrodt Chemical Works, Purity 99%

Apparatus

The apparatus is described in Figure 37.

Procedure

In a typical experiment, one gram of $KClO_3$ was placed in the Vycor

reactor and the reactor and supporting equipment were evacuated. The reactor was then filled to atmospheric pressure with N_2F_4. The potassium chlorate was then stirred with a magnetic Teflon coated stirring bar for 2-20 hours at 25°C. The products were then fractionated and analyzed.

Results

The results are summarized in Table 59, Experiments 1810D-85 and 1810D-86, and in Table 65, Experiments 1928D-26, 1928D-29 and 1928D-30.

At 25°C a reaction occurred between $KClO_3$ and N_2F_4 to form ClO_3F, nitrogen oxides, NF_3 and SiF_4. The SiF_4 was formed by inter-action of active fluorine decomposition products and/or tetrafluorohy-drazine with the Vycor reactor.

The solid generally contained small amounts of fluorine which was due to the presence of potassium fluoride. Infrared, X-ray and elemental analyses of the solid indicated that the product was a mixture of $KClO_3$ and KF.

The presence of $FClO_3$ in the gaseous product is interesting. Two possible sources for this are

(1) reaction of a fluorine atom with a liberated ClO_3 radical

$$F\cdot \ + \ ClO_3\cdot \ \longrightarrow FClO_3$$

(2) decomposition of the desired NF_2ClO_3

$$2\,NF_2ClO_3 \longrightarrow 2\,FClO_3 \ + \ N_2F_2$$

However, there was no evidence for any N_2F_2 in the product.

The presence of $FClO_3$ prompted a more thorough study of the reaction, using ultraviolet activation. The apparatus is described in Figure 12. A Hanovia No. 30600 ultraviolet lamp (1849-4000 Å) was used to promote the formation of NF_2 radicals from N_2F_4 which were expected to react with the solid $KClO_3$. The procedure was the same as described in Section VI, Ala, for the reaction of N_2F_4 with ClO_4. Results are summarized in Table 66.

Potassium chlorate was dried in a vacuum oven at 110°C for four hours prior to use. Infrared analysis showed no evidence for the presence of water.

Dry potassium chlorate does not decompose when irradiated and is stable to N_2F_4 in the absence of irradiation. In the presence of irradiation, reaction occurs with the formation of KF as a major product. In addition, volatile decomposition products such as $NOCl$, NO_2, N_2O and NOF are formed. The presence of small amounts of potassium bifluoride also was observed. This may have been due to traces of water still present in the $KClO_3$ although the latter was dry at the start. It is

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Table 65

Reactions of Tetrafluorohydrazine

Experiment Number	Reactant	Weight of Reactant g.	Weight N_2F_4 g.	Temperature °C	Time hrs.	Results
1928D-26	$KClO_3$	0.98	1.2	25	2	0.62 g. wt. increase of solids (probably due to $(NO_2)_2SiF_6$ formation from vycor reactor). IR and MS analysis of gases: N_2, NO_2, $FClO_3$, no N_2F_4. Stable solid contained neither nitrogen or fluorine.
1928D-29	$KClO_3$	1.62	1.0	25	24	No wt. increase of solid. IR analysis of gases: N_2O, NO_2, NF_3, trace N_2F_4. Recovered $KClO_3$.
1928D-30	$KClO_3$ Ultraviolet light	1.14	1.0	25	4	0.04 g. wt. loss of solids. IR analysis of gases: N_2O, NO_2, NF_3, trace N_2F_4. Recovered $KClO_3$.
1928D-37	$HClO_4$ Ultraviolet light	4.58	1.5	25	6	IR analysis of gases: N_2O, NO_2, $FClO_3$, no solids. Recovered $HClO_4$.
1928D-43	$LiClO_3$	1.36	0.9	25	1	0.25 g. wt. loss of solids. IR analysis of gases: N_2O, NO_2, NF_3, SiF_4, trace $FClO_3$, no N_2F_4. Solid analysis pending.
1928D-48	$LiClO_3$	2.16	0.9	25	2	0.34 g. wt. loss of solids. IR analysis of gases: N_2O, NO_2, NF_3, $FClO_3$, SiF_4, no N_2F_4. Solid analysis pending.

Table 66

Reaction of Irradiated N_2F_4 with $KClO_3$

Experiment No.	602-99	1602-100	1602-97	1602-98	3889-3	3889-4
N_2F_4 (g.)	1.625	0	1.762	1.610	0.527	0.795
$KClO_3$ (g.)	0.8909	0.7187	1.4254	1.0198	0.8721	0.7907
Reaction Temp. (°C)	R.T.	100-110	100-110	100-110	85-100	104-112
Reaction Period (hr.)	2	2	5	2.5	3	3
Gaseous Products						
Weight (g.)	1.507	N_2 Atmos.	2.017	1.588	0.512	0.678
I. R. Analysis	Mostly N_2F_4 Some NOF,NO_2, N_2O		NOCl,NO_2,N_2F_4 N_2,NF_3,N_2O,HNO_3, O_2	NOF,NO_2,N_2O trace N_2F_4	Mostly N_2F_4 Some NF_3,NOF. NO_2,N_2O	Mostly N_2F_4. Some NOF NO_2,NOCl NOF,N_2F_4, NO_2,NOCl
Mass Spectrum	87.41 mole%N_2F_4 12.18 mole% NOF 0.41 mole%N_2O	77.5 mole%N_2 22.5 mole%Air (Argon present)	33.4%NO_2,15.1%N_2, 19.0%O_2,23.4%NOCl 2.5%N_2F_4,2.3%N_2O 2.2%NF_3	NOF,NO_2, N_2F_4,NF_3,N_2 O_2,NO_2,N_2O, HCl	----	
Solid Products						
Weight (g.)	0.8762	0.7092	0.7321	0.5187	0.8672	0.7299
I.R. Analysis	Mostly $KClO_3$ trace KF·HF	Only $KClO_3$	No $KClO_3$ Only KF·HF	No $KClO_3$ Only KF·HF	Only $KClO_3$	Mostly $KClO_3$ Some KF·HF
X-Ray Analysis	Only $KClO_3$	----	Primarily KF Some KF·HF	-	-	-
Elemental Analysis	%Total F = 3.6 %N = 0	-	%Total F = 42.0	%Total F = 41.0 %Hyd.F = 38.9 %N = 0	-	-

conceivable that the observed products arise through the transitory formation of NF_2ClO_3, which then decomposes to the products obtained. If decomposition does occur it may be due either to the inherent instability of the molecule, or to its instability in the irradiation zone. The route to the formation of the various products may be envisaged as

$$N_2F_4 \longrightarrow NF_2 \xrightarrow{\text{U.V.}} \cdot NF + \cdot F$$

$$\cdot F + KClO_3 \longrightarrow KF + \cdot ClO_3$$

$$NF_2 \cdot + ClO_3 \cdot \longrightarrow NF_2ClO_3$$

$$[NF_2ClO_3] \longrightarrow NOF + NOCl + NO_2$$
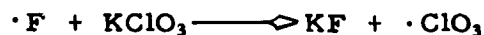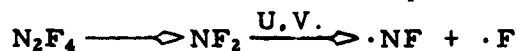
The absence of perchloryl fluoride, $FClO_3$, in the reaction products may be meaningful, since it would be an expected product if the $ClO_3\cdot$ was not immediately taken up in some way to prevent reaction with fluorine atoms.

When moist $KClO_3$ was reacted with N_2F_4 at 25°C without ultraviolet activation, $FClO_3$ was detected in the products.

It was concluded that a reaction occurs between $KClO_3$ and N_2F_4 to yield only decomposition products. If NF_2ClO_3 formed, it decomposed readily and could not be isolated.

e. N_2F_4 + KNO_3

Material

N_2F_4. E.I. DuPont de Nemours and Company, purity 99%.

KNO_3. Amend Drug and Chemical Co., U.S.P.

Apparatus

The apparatus is described in Figure 12. Possible side reactions of N_2F_4 with glass were eliminated by using only Teflon and calcium fluoride for the ultraviolet reactor, and polypropylene, copper, and stainless steel in the construction of the supporting system. A Hanovia No. 30600 ultraviolet lamp (1849-4000 Å) light source was used.

Procedure

In a typical experiment KNO_3, previously dried in a vacuum oven at 100°C for two hours, was placed in the reactor and the reactor system sealed and evacuated. The reactor and supporting system were flushed with high purity, dry nitrogen several times, evacuated, and a weighed quantity of N_2F_4 admitted to a pressure of 400 mm. The recycle trap was cooled with Dry Ice (-78°C); the bellows pump was turned on, and the reactor was irradiated for a period of two hours. The volatile products were continuously collected in the polypropylene trap while the unreacted N_2F_4 was recycled. After two hours the products were fractionated and analyzed.

Results

The results of two experiments are summarized in Table 67.

The purpose of this study was to prepare the compound NF_2NO_3 by the following reaction:

$$N_2F_4 \xrightarrow{U.V.} 2NF_2 \xrightarrow{U.V.} NF \cdot + F \cdot$$

$$F \cdot + KNO_3 \longrightarrow KF \cdot + NO_3 \cdot$$

$$NF_2 \cdot + NO_3 \cdot \longrightarrow NF_2NO_3$$
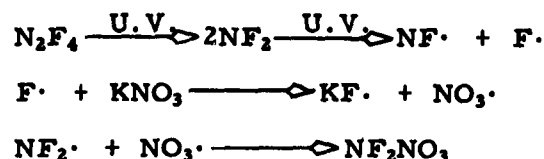
The reaction of KNO_3 with N_2F_4 with ultraviolet activation did not produce any significant products. Generally some decomposition of the N_2F_4 occurred to form NF_3, NOF and N_2O, but most of the KNO_3 was recovered unchanged. Similar results were obtained when KNO_3 was reacted with N_2F_4 in a Vycor reactor, Figure 37, at 25°C. This work is summarized in Table 59, Experiment 1810D-87.

It was concluded that the reaction of KNO_3 with N_2F_4, with or without ultraviolet activation, does not produce NF_2NO_3 or any other significant products.

f. N_2F_4 + $NaClO_2$
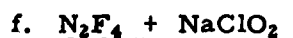
Material

N_2F_4. E.I. DuPont de Nemours and Company, purity 99%+

$NaClO_2$. Allied Chemical and Dye Corporation, Analytical Grade.

Apparatus

The apparatus is described in Figure 38. Sodium chlorite was contained in Teflon reactor "E" to minimize interaction with Pyrex glass.

Procedure

The sodium chlorite, either pure or supported by a diluent such as shredded Teflon or calcium chloride, was placed in reactor E. The N_2F_4, diluted with nitrogen, was passed through the reactor. A column around the reactor permitted cooling to be conducted although the poor heat transfer properties of the Teflon made exact temperature control difficult. Samples of the gas streams were taken during the course of the reaction and the solids were analyzed by X-ray and infrared and for elemental composition.

Results

The results of thirteen experiments are summarized in Table 68.

since, in the presence of an excess of NF_2 radicals, coupling with the ClO_2 radical could result.

It was concluded that tetrafluorohydrazine did not react with dry sodium chlorite when ultraviolet activation was not used. When moist sodium chlorite was used, chlorine dioxide was formed but $NaNF_2$ or NF_2ClO_2 either did not form or a rapid decomposition occurred so that the compounds could not be isolated. Similarly, chlorine dioxide was formed by the reaction of dry sodium chlorite with tetrafluorohydrazine activated with ultraviolet light but there was no evidence that the desired compounds $NaNF_2$ or NF_2ClO_2 were present in the final products.

g. $N_2F_4 + HClO_4$
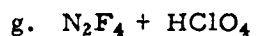
Material

N_2F_4. E. I. DuPont de Nemours and Company.

A typical analysis is:

N_2F_4	99.0 wt %
N_2O	0.40
NO	0.25
NF_3	0.18
N_2	0.12
	99.95

$HClO_4$. Anhydrous perchloric acid was prepared by the vacuum distillation of a mixture of 70% perchloric acid and 20% fuming sulfuric acid by a method analogous to that reported by Smith (62) in the apparatus described in Figure 39. Yields of 25-29 g. were obtained by distilling a mixture of 35 ml. 70% perchloric acid and 120 ml. of 20% fuming sulfuric. The anhydrous perchloric acid was distilled under full vacuum over the temperature range of 30-75°C during a two hour period; the main portion distilling between 45-60°C.

Apparatus

Gas phase reactions were conducted in the apparatus described in Figure 40. Reactions in the liquid phase were conducted in a one-litre stainless steel cylinder which was attached to a typical material transfer line described in Figure 14. In some experiments a Teflon reactor described in Figure 15 was used.

Procedure

In a typical liquid phase reaction, 400 ml. of carbon tetrachloride containing 5 ml. of anhydrous perchloric acid was placed in the stainless steel or Teflon reactor. The reactor was cooled to -78°C, evacuated, and pressured with 7 grams of N_2F_4. After standing at 25°C for two hours,

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hydrolyzable fluoride. The following compositi n would account for all
of the materials present in the solid product.

$NaClO_3$	50.5%
$NaF \cdot HF$	22.2%
NaF	11.0%
$NaCl$	17.3%

Infrared examination in conjunction with mass spectrometric analysis
revealed that the gaseous products were composed of NO_2F, NOF, NO_2,
ClO_2, NF_3 and O_2.

These products could have arisen from a variety of reactions.
The formation of sodium bifluoride could be accounted for by the presence
of a small amount of water in the starting sodium chlorite. It is interesting
to note that the products which resulted from the U.V. irradiation study
were somewhat different from those observed with moist sodium chlorite
and tetrafluorohydrazine.

$$NaClO_2 + N_2F_4 \xrightarrow{U.V.} NaClO_3 + NO_2F + NOF + NO_2 + ClO_2 + NF_3 + O_2$$

$$NaF \cdot HF + NaF + NaCl$$

$$NaClO_2\,(moist) + N_2F_4 \longrightarrow NaClO_3 + ClO_2 + NO_2Cl + Nitrogen\ Oxides +$$

$$NaCl$$
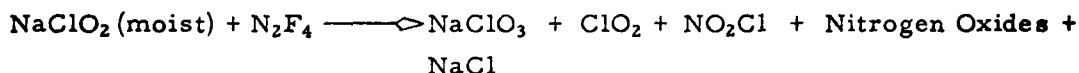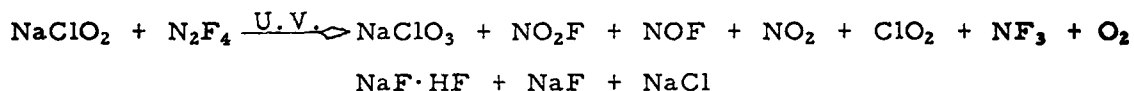
Sodium fluoride was not formed in the absence of irradiation, suggesting
that irradiation did lead to the formation of fluorine radicals which re-
acted with the sodium chlorite to produce sodium fluoride. The gaseous
products could be partially accounted for by the formation and decomposi-
tion of the desired NF_2ClO_2. The presence of sodium chlorate and chloride
is probably due in part to the known isomerization of sodium chlorite on
the application of heat (61).

$$3\,NaClO_2 \longrightarrow 2\,NaClO_3 + NaCl$$
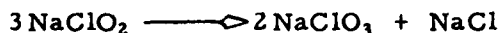
Since the ratio of sodium chlorate to sodium chloride found was greater
than 2, the excess sodium chlorate was probably formed as a result of
some oxidation of the sodium chlorite by the nitrogen oxides. The forma-
tion of sodium fluoride suggests that the initial reaction steps may be:

$$NF_2 \xrightarrow{U.V.} NF \cdot + F \cdot$$

$$F \cdot + NaClO_2 \longrightarrow NaF + ClO_2 \cdot$$

$$NF \cdot + NaClO_2 \longrightarrow NaF + ClO_2 + 1/2\,N_2$$
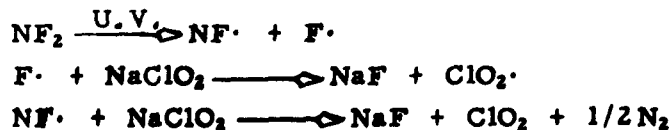
This can then be followed by a number of reactions to account for some
of the products. The transitory formation of NF_2ClO_2 would be predicted

Low fluorine content indicated that very little, if any, sodium fluoride was being formed. The absence of nitrogen eliminated the possibility of even trace amounts of NF materials in the solid. The major solid product appeared to be sodium chloride and some sodium chlorate. A material balance on the fluorine was not made but nitrogen trifluoride was the only fluorine containing product identified.

Although no direct evidence for the formation of sodium difluor-amine was obtained, the absence of sodium fluoride suggests that $NaNF_2$ might have formed and then reacted with the chlorine dioxide generated from the same reaction.

$$1/2 \ N_2F_4 + NaClO_2 \longrightarrow NaNF_2 + ClO_2$$

$$3 \ NaNF_2 + 3 \ ClO_2 \longrightarrow 3 \ NaCl + 2 \ NF_3 + NO_2 + 2 \ O_2$$

It is possible that the reaction is simply oxidation of N_2F_4 by $NaClO_2$, but the absence of significant amounts of fluoride ion would be difficult to explain.

Since this reaction resulted in the formation of ClO_2 it was thought that under the proper conditions either $NaNF_2$ or NF_2ClO_2 might be isolated from the products. It was decided that the reaction of ultraviolet activated tetrafluorohydrazine and dry sodium chlorite would provide more reliable data.

The apparatus used in this study is described in Figure 12. A Hanovia No. 30600 ultraviolet lamp (1849-4000 Å) was used to activate the tetrafluorohydrazine.

In a typical experiment 0.63 grams of dry sodium chlorite was placed in the reactor and 0.36 grams of N_2F_4 was added to the evacuated system producing a pressure of 375 mm. No evidence of reaction was observed for a period of a few minutes and then the unfiltered Hanovia No. 30600 U.V. lamp was turned on, the entire system being enclosed by aluminum foil.

Within ten minutes after the lamp had been turned on a pressure increase amounting to approximately 100 mm. was observed which was then followed by a rapid pressure decrease. The pressure of the system was 300 mm. after 15 minutes of irradiation and at this point the lamp was turned off and the gaseous products which had not condensed in the trap at -78°C were collected at -196°C. Approximately 50 mm. of non-condensable gas was present. The solid products and the condensable gaseous materials were then isolated and analyzed.

The infrared spectrum of the solid product in a Nujol mull showed sodium chlorate and sodium bifluoride, but no sodium chlorite. X-ray diffraction identified sodium chlorate, sodium chloride, sodium fluoride and sodium bifluoride as being present. Elemental analysis of the material showed 20.3% hydrolyzable F, 27.37% total Cl, 10.50% hydrolyzable Cl, and a trace of nitrogen. Total fluoride was not greater than the

The reaction of chlorine dioxide with tetrafluorohydrazine is a vigorous reaction and ignition (58, 59) or the formation of nitrogen oxides at low temperatures (60) has been observed. It has also been reported that tetrafluorohydrazine reacts with sodium chlorite at higher temperatures to produce nitrosyl chloride and nitrogen tetroxide.

In an exploratory experiment involving sodium chlorite and tetrafluorohydrazine, it was found that chlorine dioxide was liberated and the N_2F_4 was completely consumed. The reaction of chlorine with sodium chlorite is a well known commercial process for the preparation of chlorine dioxide.

$$Cl_2 + NaClO_2 \longrightarrow ClO_2 + NaCl$$
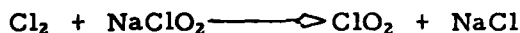
It was expected that an analogous reaction with tetrafluorohydrazine would occur:

$$N_2F_4 + NaClO_2 \longrightarrow ClO_2 + NaNF_2$$

The reaction of N_2F_4 with moist sodium chlorite produces chlorine dioxide. In the absence of moisture no reaction occurs under ambient conditions. The moisture apparently is not decomposing the N_2F_4 to NOF and other reaction conditions; N_2F_4 is stable to water at room temperature and can be recovered unchanged. This characteristic of $NaClO_2$ appears to be generally true since chlorine also does not react with dry $NaClO_2$.

The reaction with N_2F_4 is temperature dependent since, at 0°C, no noticeable reaction occurs whereas at 18°C the reaction is vigorous. Attempts were made, without notable success, to limit the exothermicity of the reaction by the incorporation of Teflon shavings as a heat sink. Calcium chloride, however, appears to work well in this capacity. Infrared examination of the gases indicates that chlorine dioxide is immediately released and this is very soon followed by a mixture of products including NO_2, NOCl, NF_3 and NO_2Cl along with the ClO_2. The solid products which remain behind include NaCl, $NaClO_2$ and $NaClO_3$. Analysis by X-ray did not establish the presence of sodium fluoride. The solids did not oxidize neutral potassium iodide and infrared examination did not show the presence of any unexplained peaks. The elemental compositions of the solid products were somewhat surprising. The analyses of two typical solid products are shown below:

Sample No.	P-472-2	P-471-1
Total Chlorine	41.22	44.89
Hydrolyzable Chlorine	28.84	26.70
Total fluorine	1.87	0.19
Hydrolyzable fluorine	0.31	0.0
Total nitrogen	0.0	0.0
Water	13.32, 13.69	12.09, 11.90

TABLE 68

Reactions of $NaClO_2$ with N_2F_4

Rx. No.	N_2F_4 (g)	$NaClO_2$ (g)	H_2O	Temp.	Conditions	Products (I.R.;X-ray)
1)	1.12	1.99	3.5%	25°C	N_2 purge	$ClO_2, N_2F_4, NaClO_3$ $NaClO_2, NaCl$
2)	1.02	1.73		-80°C	"	No reaction
3)	0.71	1.55	3.6%	-80°C	"	No reaction
4)	0.77	1.40	3.6%	-10°C	"	No reaction
5)	?	2.70	4.5%	0°C	"	No reaction
6)	0.31	2.62	4.8%	25°C	"	ClO_2
7)	0.31	0.76	4.7%	25°C	"	$ClO_2, NOCl, NO_2$
8)	0.62	2.26	4.7%	25°C	"	$ClO_2, NF_3, NOCl,$ $NO_2, NaClO_3$
9)	0.45	0.96	5.0%	25°C	"	NO_2, NO_2Cl, N_2F_4 $NaClO_3$
10)	1.00	2.24	5.0%	25°C	"	ClO_2, NO_2Cl, NO_2
11)	1.55	2.18	6.0%	20°C	$CaCl_2$ dil N_2 purge	ClO_2, NO_2Cl, NF_3
12)	?	2.55	3.5%	20°C	$CaCl_2$ dil N_2 purge	ClO_2
13)	1.03	2.50	15.0%	18°C	$CaCl_2$ dil N_2 purge	$ClO_2, NaClO_3,$ $NaClO_2$

Figure 38

Apparatus for Reaction of NaClO$_2$ with N$_2$F$_4$

A. Inlet for N$_2$F$_4$
B. N$_2$
C. Vac. Gauge
D. Stainless Steel Trap
E. Teflon Reactor
F. Vac. Pressure Gauge
G. I.R. Cell inlet
H. Glass trap
I. Glass trap
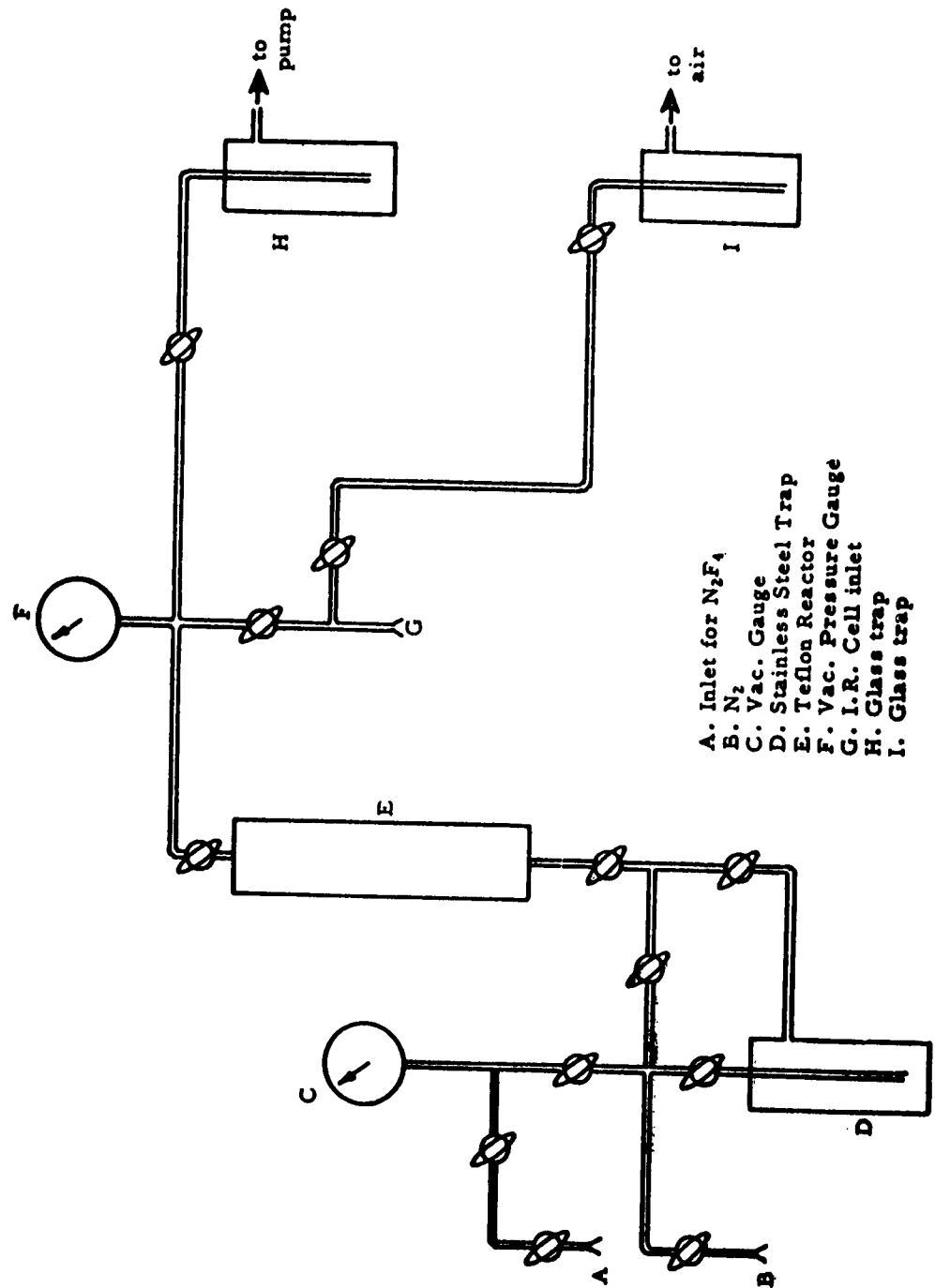
Table 67

Reaction Between U.V. Irradiated N_2F_4 and KNO_3

Experiment No.	1801 - 11[*]	1801 - 12	
Reactants			
KNO_3 (g.)	0.6785	0.4885	
N_2F_4 (g.)	0.526	1.109	
Reaction Time (Hr.)	2	4	
Reaction Temp. (°C)	R.T.	∼ 100	
Products			
Gases (g.)	0.508	0.925	
I.R. and Mass Spectrum Show	$N_2F_4 \cong 90\%$	$N_2F_4 \cong 79\%$	I.R. Identifying bands
	$NOF \cong 9\%$	$NF_3 \cong 10\%$	$N_2F_4 = 9.9, 10.4, 13.6\mu$
	$N_2O \cong 1\%$	$NOF \cong 9\%$	$NF_3 = 9.7, 11.0\mu$
		$N_2O \cong 2\%$	$NOF = 5.4-5.5\mu$ doublet 12.4, 13.1μ
Solids	0.6947	0.4979	$N_2O = 4.5, 7.8\mu$
I.R. Shows	KNO_3 only	KNO_3 only	

[*] Not Irradiated With U.V.

Figure 39

Apparatus for Preparation of Anhydrous Perchloric Acid
G. F. Smith   J. Am. Chem. Soc.   75, 184 (1953)

Figure 40

Gas Phase Reaction System N_2F_4 - $HClO_4$

the contents of the reactor were removed. A solid, insoluble in carbon tetrachloride was collected, dried by vacuum, and analyzed.

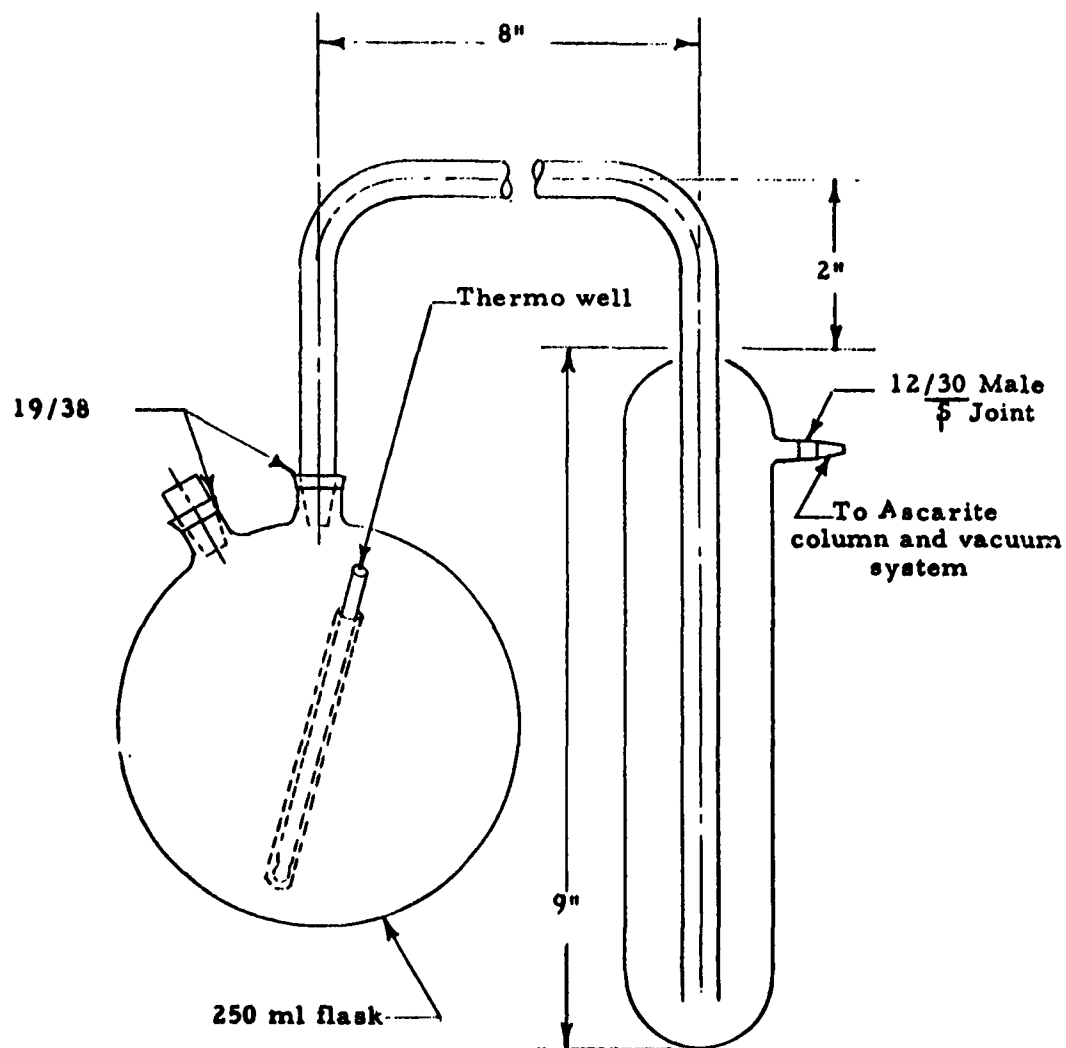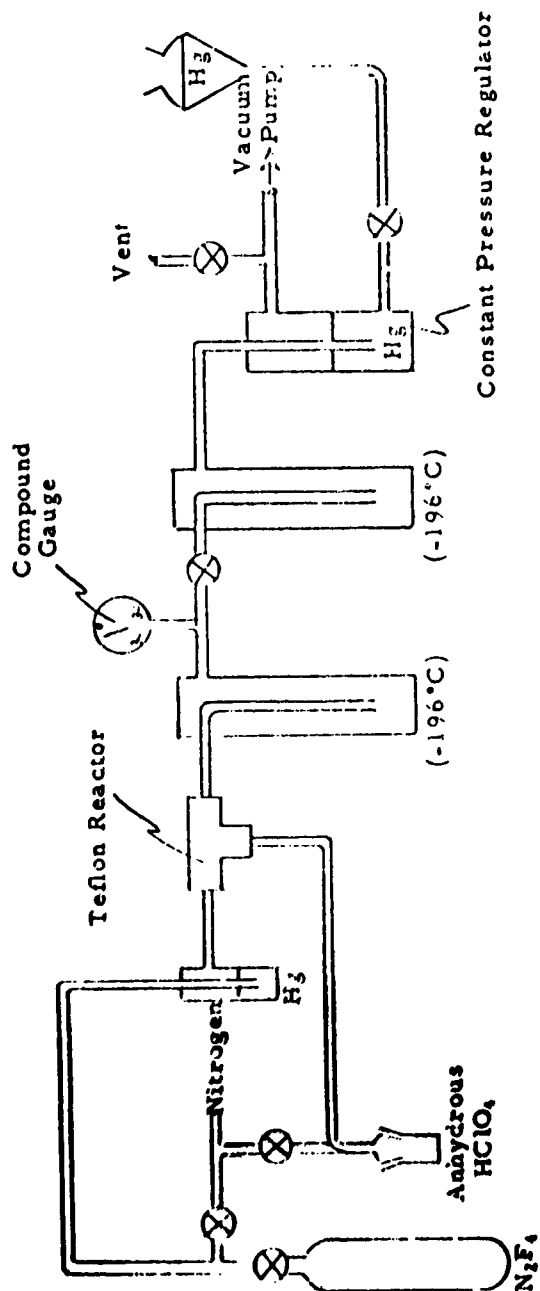Vapor phase reactions were conducted in the apparatus described in Figure 40.

In a typical reaction, approximately 1 g. of anhydrous perchloric acid is transferred in a dry box to the glass container and closed with a glass stopper fitted with a Teflon sleeve. This sleeve serves to reduce the chance of detonation caused by friction when the stopper is removed.

The container is removed from the dry box and connected to the reaction system which is then purged with a stream of nitrogen. The mercury level in the constant pressure regulator is adjusted and approximately 4 g. of N_2F_4, diluted with nitrogen, is allowed to flow through the system. The $HClO_4$ is then distilled over the temperature range 32-48°C for one hour, the vapors being carried in a stream of nitrogen into the Teflon-tee reaction chamber containing the N_2F_4. The valve to the N_2F_4 cylinder is then closed and the gaseous reaction products, collected in the -196°C trap, transferred to the receiving cylinder. The gaseous products are warmed to room temperature and samples removed for analysis. The apparatus is disassembled and the white solid deposited on the walls is transferred to a polypropylene container under an inert atmosphere.

Results

The reaction of anhydrous perchloric acid with tetrafluorohydrazine was investigated rather extensively for several reasons.

1. It could lead to the desired product NF_2ClO_4 by the following reactions:

$$N_2F_4 + HClO_4 \longrightarrow NF_2ClO_4 + NF_2H$$

or $$N_2F_4 + HClO_4 \longrightarrow NF_2ClO_4 + 1/2\,N_2F_2 + HF$$
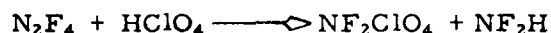
Difluoramine NF_2H, N_2F_2 and HF are relatively stable compounds, and their formation might serve as a driving force to force the reaction to completion.

2. Chlorine heptoxide is known to exist in equilibrium with perchloric acid (63)

$$Cl_2O_7 + H_2O \rightleftharpoons 2\,HClO_4$$
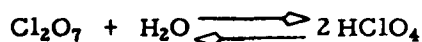
In Section IV, A.1.a, the reaction of Cl_2O_7 with N_2F_4 resulted in the formation of a solid product which was initially thought to be NF_2ClO_4. However, in later experiments these results could not be duplicated and the possibility that the reaction actually involved $HClO_4$ rather than Cl_2O_7 with N_2F_4 was not resolved. A thorough study of the reaction of $HClO_4$ with N_2F_4 was expected to provide valuable data on the possible synthesis of NF_2ClO_4.

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The results of reactions of N_2F_4 with $HClO_4$ in CCl_4 are summarized in Tables 69 and 70. Comparison of the data in these tables shows that the fluorine content of the solid product is not reproducible. This is illustrated by variations in fluorine content which ranged from 0 to 20 weight per cent. This alone was a disturbing factor since this indicates that certain unknown variables are involved and, further, the solid contains a component which does not contain fluorine at all. This substance was identified as $NOClO_4$ by X-ray analysis.

It was hoped that the variables that control the formation of high fluorine solid product could be defined by a statistical analysis of the variables water, temperature, and the presence of metals. A series of eight experiments was completed.

In all eight experiments the fluorine content of the solid product was so low as to practically exclude any fluorine containing component, especially a product such as NF_2ClO_4. An inspection of the data did not reveal a correlation of reaction time with yield, since the experiments conducted for two hours gave similar yields, in general, to those lasting as long as twenty-four hours. Experiments that were conducted in stainless steel reactors gave slightly increased yields of solid fluorine containing product over those from Teflon reactors. This is to be expected if metal containing fluorides are formed.
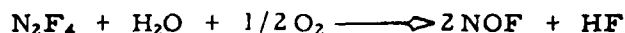
The consistent formation of $NOClO_4$ leads to the conclusion that one of the primary reactants, viz., tetrafluorohydrazine, is undergoing a reaction to form NOF which subsequently reacts to form $NOClO_4$.

The facile conversion of N_2F_4 to NOF in the presence of labile oxygen is known(65).

$$N_2F_4 + H_2O + 1/2 O_2 \longrightarrow 2NOF + HF$$

(In the absence of oxygen, only NO and HF are formed.) Subsequent reaction of the NOF with $HClO_4$ could then produce the $NOClO_4$.

These experiments point to the conclusion that the reaction of perchloric acid with tetrafluorohydrazine in carbon tetrachloride, under static conditions, does not lead to the desired product.

Yet, in experiment 28a, Table 69, the solid product contained 11.7 weight per cent fluorine of which only 0.6 weight per cent was hydrolyzable. X-ray analysis indicates that the solid contained $NOClO_4$, but the nature of the fluorine could not be explained. If the fluorine were present as a metal fluoride, it would have hydrolyzed to the fluoride ion as observed in the other experiments. This product was consumed before further analysis could be completed and the product could not be duplicated in subsequent experiments.

It was reasoned that, if the reaction of perchloric acid with tetrafluorohydrazine requires the initial formation of NF_2 radicals to form

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TABLE 69

Reaction of Anhydrous Perchloric Acid with Tetrafluorohydrazine*

Experiment No.	HClO₄ (g.)	N₂F₄ (g.)	Reaction Time (hrs.)	Product (g.)	Fluorine Total %.	Fluorine Hydrolyzable %.	Remarks
1462 - 28a	8.5	7.0	2	5.3	11.7	0.6	X-Ray indicates primarily NOClO₄
-28b	8.5	7.0	20	4.7	4.28		
-30a	7.7	7.0	2	2.3	1.0	0.6	X-Ray indicates primarily NOClO₄
-30b	7.4	7.0	2	3.8	2.61		
-30c	9.3	7.0	2	3.6	2.22		
-31a	10.9	8.0	2	5.8	7.82		
-31b	12.0	8.0	2	4.0	3.0	2.5	
-62d**	8.8	5.0	18	2.0	2.0	1.4	
-62e	8.8	5.0	18	3.9	3.3	1.9	
-62f	8.8	5.0	18	5.4	3.0	.	
-64a	15.9	4.5	20	8.8	3.5		
-64b	3.5	13	20	2.5	5	4.5	

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* All experiments were performed at room temperature in one-liter, 304 stainless steel cylinders. The solvent for each experiment was 400 ml. of carbon tetrachloride.

TABLE 70

Reactions of N_2F_4 with $HClO_4$

Expt. No.	Wt. $HClO_4$ (g.)	Wt. N_2F_4 (g.)	Wt. CCl_4 (g.)	Reactor	Wt. solid (g.)	Wet Chemical analysis of solids	Instrumental analysis of solids or gases
1516-37 *	4.15	5.945	672	Teflon	3.974	%F=3.1, %Cl=28.83 %N=5.08	X-ray - $NOClO_4$
1516-39 **	4.15	6.225	672	Teflon	3.811	%F=9.98	
1516-41	8.31	6.795	640	S.S.	2.604	Tot.F=20.24 Ionic F=20.13 %F=8.7	Paper Chromo- ClO_4^-, NO_3^-, F^- Unidentified spot
1516-43a	7.83	7.373	640	S.S.	4.213	%Tot.F=0.49 %Hyd.F=0.30	
1516-43B ***	8.32	6.920	640	S.S.	4.645	%Tot.F=4.5 %Hyd.F=3.7	
1516-45	8.00	6.675	640	Teflon	4.296	%Tot.F=1.8 %Hyd.F=2.0	IR analysis of gas NO_2, NOF, NO_2F, NF_3, N_2F_4
1516-48	(Anhyd.) 5.65	4.608	0	Teflon	0.747	%F=0, Cl=25.6 %N=2.37	
1516-50	(Anhyd.) 2.08	4.368	0	Teflon	EXPLOSION		

* = 0.498 g. $KF \cdot 2H_2O$ ** = 0.490 g. anhyd. KF   *** = 1% Chloral hydrate in $HClO_4$

NF_2ClO_4, then the reaction would proceed more readily in the vapor phase.

A series of experiments was conducted in the apparatus described in Figure 40 in which vapors of anhydrous perchloric acid and tetrafluorohydrazine were reacted in a Teflon "T" and the products were quenched in a trap cooled to -196°C.

A preliminary distillation of the perchloric acid revealed that 1 g. could be distilled under a constant pressure of 25 mm. (Hg) over the temperature range 32-43°C during a period of 50 minutes.

The gas phase reaction of N_2F_4 with anhydrous $HClO_4$ yielded 0.1 to 0.2 g. of a white solid product which was found to contain free mercury. This free mercury apparently was carried on the N_2F_4-N_2 stream from the mercury flow meter into the Teflon-"tee" reactor. The white solid also contained 0.4% total fluorine by weight. X-ray diffraction of this solid material could not establish the presence of $NOClO_4$ nor any mercury compounds. Although the analysis was not conclusive, the white solid was probably a mixture of $NOClO_4$, HgF_2, Hg and HF, either as an adduct or mechanically absorbed.

Infrared examination of the gaseous products collected at -196°C revealed that the N_2F_4 had been almost totally decomposed, leading to the formation of NF_3, NO_2, N_2O and NOF.

The desired reaction

$$N_2F_4 + HClO_4 \xrightarrow{\quad\diagup\diagdown\quad} NF_2ClO_4 + HF + 1/2N_2F_2$$

apparently did not occur since evidence for NF_2ClO_4 and N_2F_2 in the products was never established.

When all of the data obtained in liquid phase reactions of anhydrous perchloric acid with tetrafluorohydrazine as well as the vapor phase reactions was considered, rigorous conclusions could not be made regarding the possible formation of NF_2ClO_4.

Complete characterization of any one product mixture was complicated because:

1. The mixtures were unstable, with fluorine being lost merely on standing in a closed system.

2. NMR examination could not be used because the metals present interfered with the fluorine signal.

3. Infrared examination was of limited value because the mixtures reacted with the KBr pellets and with Nujol when mulls were attempted.

4. X-ray examination showed the presence of both crystalline and amorphous components.

Nevertheless, no evidence could be found suggesting the presence of an N-F bond.

It is conceivable that small amounts of oxygen from the partial decomposition of $HClO_4$ could alter the reaction considerably. This might result in the formation of only small amounts of NF_2ClO_4 with the rest of the product contaminated by large quantities of $NOClO_4$ and metal fluorides. The following reaction sequence illustrates what could occur. Steps (1) and (2) have been previously suggested by Thiokol, Reaction Motors Division (109).

(1) $\quad F_2N - NF_2 + 1/2 O_2 \longrightarrow F_2N - NF_2(O)$

(2) $\quad F_2N(O) - NF_2 \longrightarrow NOF + F\cdot + NF_2\cdot$

(3) $\quad NOF + HClO_4 \longrightarrow NOClO_4 + HF$

(4) $\quad F\cdot + HClO_4 \longrightarrow HF + ClO_4\cdot$

(5) $\quad ClO_4\cdot + NF_2\cdot \longrightarrow NF_2ClO_4$

(6) $\quad F\cdot + NF_2\cdot \longrightarrow NF_3$

(7) $\quad NOF + HF \longrightarrow NOF\cdot HF$

(8) $\quad Fe + 3F\cdot \longrightarrow FeF_3$
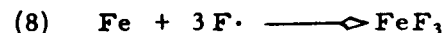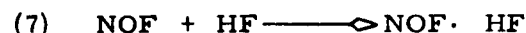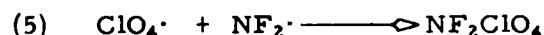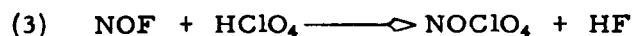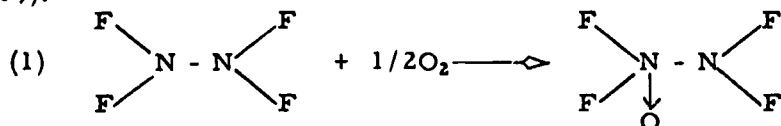
In summation, it can be stated that a reaction occurs between anhydrous perchloric acid and tetrafluorohydrazine at 25°C to yield a solid product. The solid contains as a major component $NOClO_4$. The overall reaction is complex and interaction can occur with metal systems to form metal fluorides. The desired compound NF_2ClO_4 was not detected in the products of this reaction.

h. $N_2F_4 + NH_4ClO_4$

Material

N_2F_4. E. I. DuPont de Nemours and Company, purity 99% +

NH_4ClO_4. The Matheson Company Inc., Reagent Grade.

Apparatus

An all metal apparatus used in this study is described in Figure 41. Ammonium perchlorate was held in a polyethylene boat.

Procedure

In a typical experiment, one gram of ammonium perchlorate was placed in a polyethylene boat and the boat was placed in the apparatus as

NH-2090

Figure 41

Apparatus for Reaction of N_2F_4 with NH_4ClO_4

Pressure Gauge

SS

SS

SS

-196°C trap

-78°C trap

-22°C trap

to vac
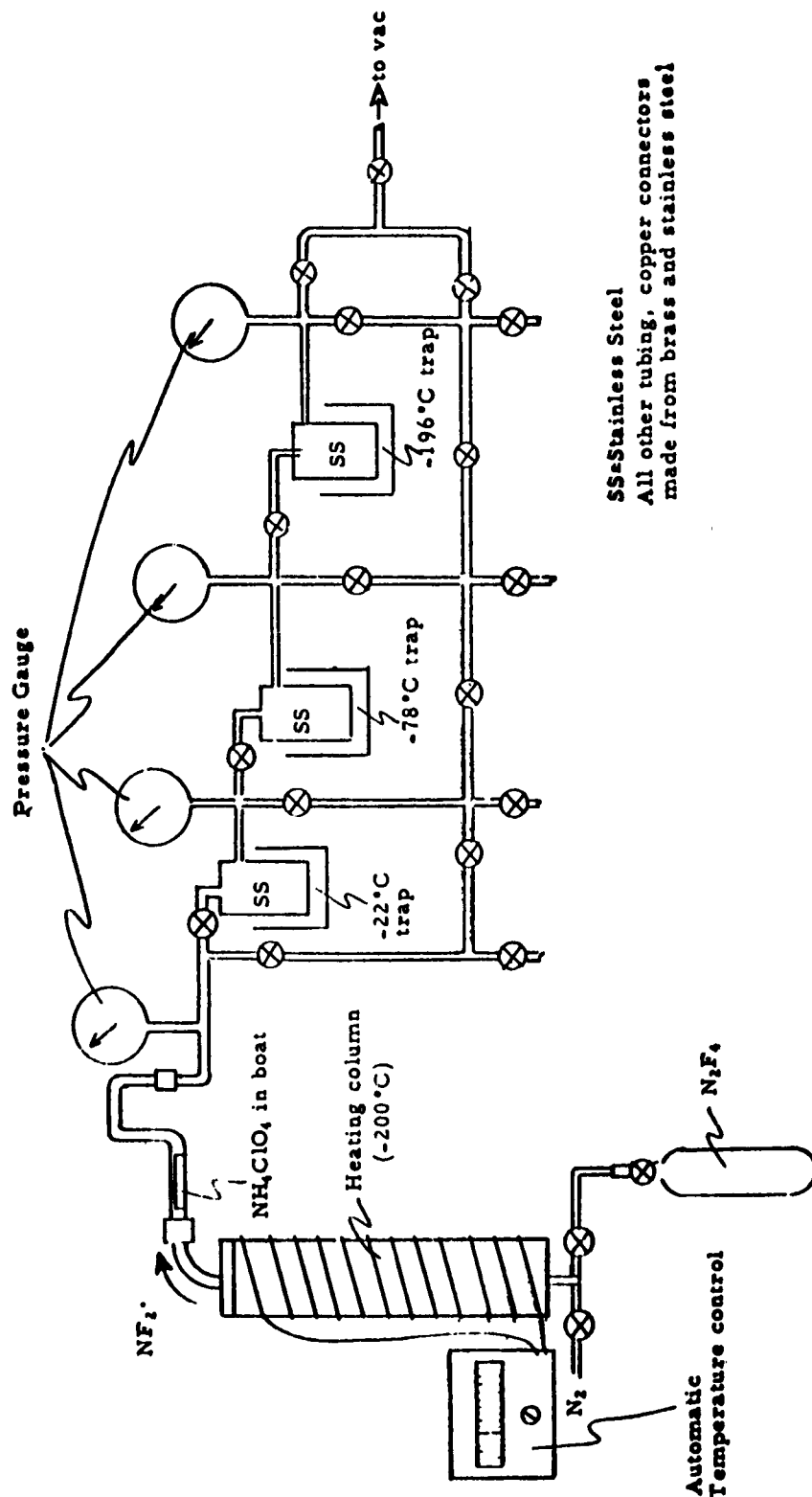
SS=Stainless Steel
All other tubing, copper connectors
made from brass and stainless steel

NH_4ClO_4 in boat

Heating column
(~200°C)

NF_3

N_2F_4

N_2

Automatic
Temperature control

described in Figure 41. The system was then evacuated, closed, and a gas stream of N_2F_4, preheated to 200°C, was slowly diffused over the ammonium perchlorate until a pressure of one atmosphere developed in the system. The gaseous products were then collected in low temperature traps, fractionated, and analyzed. The solid product remaining in the polyethylene boat was weighed and analyzed.

Results

This exploratory work was conducted to determine whether thermally activated NF_2 radicals would extract hydrogen from ammonium perchlorate with addition of NF_2 groups to the nitrogen, according to the equation:

$$2NF_2\cdot \ + \ NH_4ClO_4 \longrightarrow \left[NF_2 - NH_3\right]^+ClO^-_4 \ + \ HF \ + \ 1/2\,N_2F_2$$
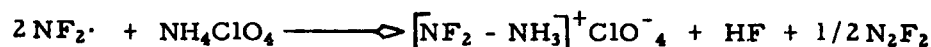
There was no evidence of a reaction between thermally activated N_2F_4 (200°C) and solid ammonium perchlorate. There was no change in weight of the ammonium perchlorate and analysis showed no fluorine in the recovered solid. Recovered gaseous products consisted mainly of N_2F_4 with only trace amounts of NF_3, NOCl, and NO_2. Some air undoubtedly leaked into the evacuated system and caused decomposition of small amounts of N_2F_4.

It was concluded that NF_2 radicals thermally activated to 200°C do not react with solid ammonium perchlorate.

i. $N_2F_4 \ + \ Cl_2$

Materials

N_2F_4. E.I.DuPont de Nemours and Company, purity 99% +

Cl_2. The Matheson Company Inc., purity 99.8%

Apparatus

This reaction was investigated in the electric discharge apparatus described in Figure 35 and the microwave apparatus described in Figure 34.

The electric discharge apparatus was constructed entirely of Pyrex glass except for the electrodes which consisted of two copper plates.

In the microwave apparatus the reactor consisted of a Teflon tube with the supporting vacuum line constructed of monel traps interconnected with copper tubing. Microwave energy was supplied with a Raytheon Microtherm Unit, Model KV-104A, with a maximum power of 100 watts at 2450± 25 megacycles.

Procedure

In a typical experiment utilizing the electric discharge apparatus, the system was evacuated and the discharge was started. The reactants

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were metered through differential pressure capillary flowmeters into the
discharge tube and the products were collected in traps cooled to -196°C.

In a typical microwave discharge experiment, the system was
evacuated and the discharge was initiated with a Tesla coil. The reactor
tube was cooled by passing ambient air over the discharge zone. The
reactants were metered through calibrated flowmeters and the products
were collected in traps cooled to -196°C.

Results

The objective of this study was to determine whether NF_2Cl could
be prepared in a one step process by microwave or electric discharge
activation of tetrafluorohydrazine and chlorine:

$$N_2F_4 + Cl_2 \longrightarrow 2NF_2Cl$$

The results of the electric discharge experiment are summarized
in Table 60, Experiment 1810D-52. There was no evidence for the forma-
tion of NF_2Cl. Volatile products consisted of Cl_2, SiF_4, NO_2 and possibly
NO_2F. All of the N_2F_4 was decomposed either by interaction with Pyrex
glass or the electric discharge.

The results of the microwave activated reaction of N_2F_4 and Cl_2
are summarized in Table 58, Experiment 1810D-62. There was no
evidence for the presence of NF_2Cl in the gaseous products which con-
sisted of N_2F_4, Cl_2, CF_4, CF_3, and N_2O. Some decomposition of the
Teflon occurred as a result of the microwave activation. Not all of N_2F_4
was decomposed in this case.

It was concluded that microwave or electric discharge activation
of N_2F_4 and Cl_2 results mainly in the decomposition of the N_2F_4, but NF_2Cl
is not formed under the conditions employed.

j. $N_2F_4 + ClF_3$

Material

N_2F_4. Stauffer Chemical Company, purity 93%.

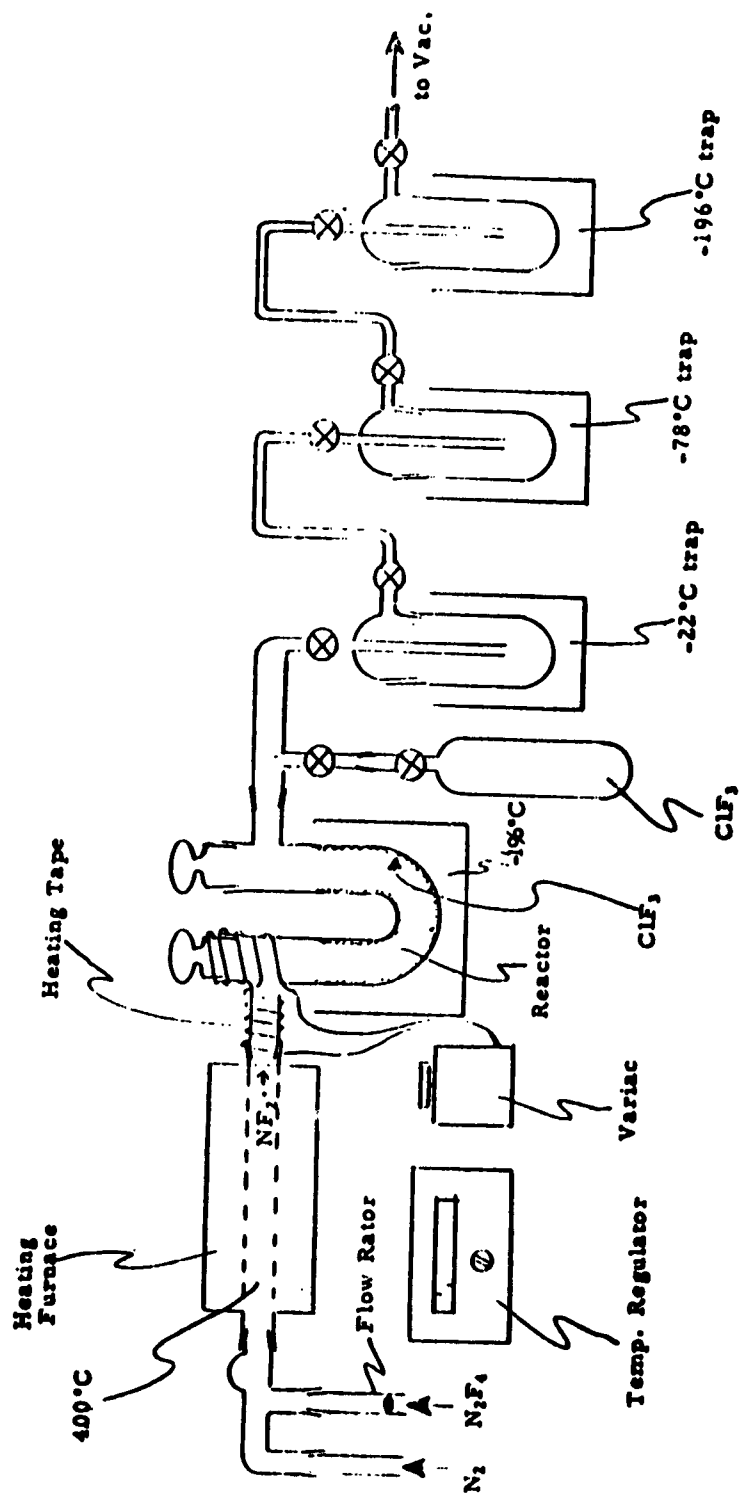ClF_3. The Matheson Company Inc.

Apparatus

The reactor and supporting apparatus were constructed entirely of
Pyrex glass, as described in Figure 42.

Procedure

The system was evacuated and approximately one gram of ClF_3
was expanded into the U-tube reactor. The reactor was then quickly

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FIGURE 42

Reaction System: N_2F_4 - ClF_3

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quenched with a -196°C liquid nitrogen bath to solidify the ClF_3 evenly on the reactor walls. With the reactor temperature held at -196°C, approximately one gram of N_2F_4 was slowly diffused through a 400°C heating column into the reactor. The active NF_2· radicals generated by this high temperature method were thus allowed to react with the solid ClF_3. After the addition of the NF_2· radicals, the -196°C bath was removed and the reactor allowed to warm to room temperature. The effluent gases from the reaction were fractionated by vacuum distillation and samples collected for analysis.

Results

The reaction of tetrafluorohydrazine with chlorine trifluoride was investigated as a method for preparing the hypothetical compound $Cl(NF_2)_3$. The substitution of NF_2 groups for fluorine in the ClF_3 molecule could possibly occur according to the following equation:

$$3 N_2F_4 + ClF_3 \longrightarrow Cl(NF_2)_3 + 3 NF_3$$

Two exploratory reactions were conducted to investigate the behavior of this system.

Of primary concern in this method was the proper dissipation of the heat accompanying the reaction, thus preventing the desired product formed from reacting further. The reaction zone therefore was kept at a low temperature to facilitate isolation of any new compound of unknown stability.

No new compounds, however, were identified in the reaction products. A reaction did occur, leading only to the series of decomposition products listed below. The formation of SiF_4, $(NO)_2SiF_6$ and $NOBF_4$ again points to the hindering and unwanted side reaction of N_2F_4 with glass.

REACTION OF N_2F_4 WITH ClF_3

Expt. No.	Fractionation of Gaseous Products -22°C	-78°C	-196°C	Solid Products	Remarks
1535-86-1	-	-	NOCl NO_2 SiF_4 C_2F_6 * SF_6 *	-	* Impurities initially present in N_2F_4
1535-86-2	NO_2 SiF_4 NOCl** SF_6	NO_2F HNO_3 C_2F_6 * SiF_4 ClO_2**	NO_2 NOCl SiF_4 SF_6*	NO^+*** $SiF_6^=$ BF_4^-	**Trace amounts present only ***Mixture of $(NO)_2SiF_6$ and $NOBF_4$

In view of the complicating side reactions in the glass system the reaction of ClF_3 with NF_2 radicals was investigated in an all Teflon apparatus described in Figure 23.

In this study 1.314 grams of ClF_3 (purified by distilling the ClF_3 over NaF at 100°C to remove HF) was placed in the Teflon coil R_3, and the ClF_3 slowly distilled into a second Teflon coil R_4 through a Teflon "T" where the ClF_3 was mixed with a stream of N_2F_4 ($\sim$ 7g) previously heated to 195°C at 5mm pressure. The unreacted ClF_3 and N_2F_4 and/or products were quenched rapidly in the Teflon coil R_4 at -196°C. When the distillation was complete the products were fractionated and analyzed.

There was no evidence for a reaction. Except for minor handling losses most of the N_2F_4 and ClF_3 were recovered. The complete absence of even trace quantities of NF_3 indicated that the expected reaction did not occur even when the N_2F_4 was heated to 195°C.

This study in an all Teflon system emphasizes the necessity of using inert material for investigating reactions with highly active fluorine compounds.

It was concluded that ClF_3 vapors and NF_2 radicals generated at 195°C and approximately 5 mm pressure do not react in a Teflon system to form NF_3 and $Cl(NF_2)_3$. The reactants were recovered.

k. $N_2F_4 + N_2O_4$

Material

N_2F_4. E.I. DuPont de Nemours and Company, purity 99%[+].

N_2O_4. The Matheson Company Inc. No detectable impurities by infrared.

Apparatus

The apparatus is described in Figure 43. A Teflon "T" served as the reactor. This reactor was connected to two Teflon tubing coils and a Teflon NMR tube as depicted in Figure 43. The apparatus was constructed of Teflon, stainless steel, and copper tubing. Only that portion of the apparatus used for discarding or venting volatile products was constructed of Pyrex glass.

Procedure

In a typical experiment, a stream of NF_2 radicals generated by heating N_2F_4 to 185°C at < 1 mm pressure was reacted with a stream of NO_2 radicals in the Teflon "T". A portion of the product was condensed directly into a Teflon NMR tube cooled to -196°C to prevent decomposition of unstable compounds while the major portion of the products was condensed into the Teflon coil R_4 for subsequent fractionation and analysis.

Figure 43

APPARATUS FOR REACTION OF $N_2O_4 + N_2F_4$
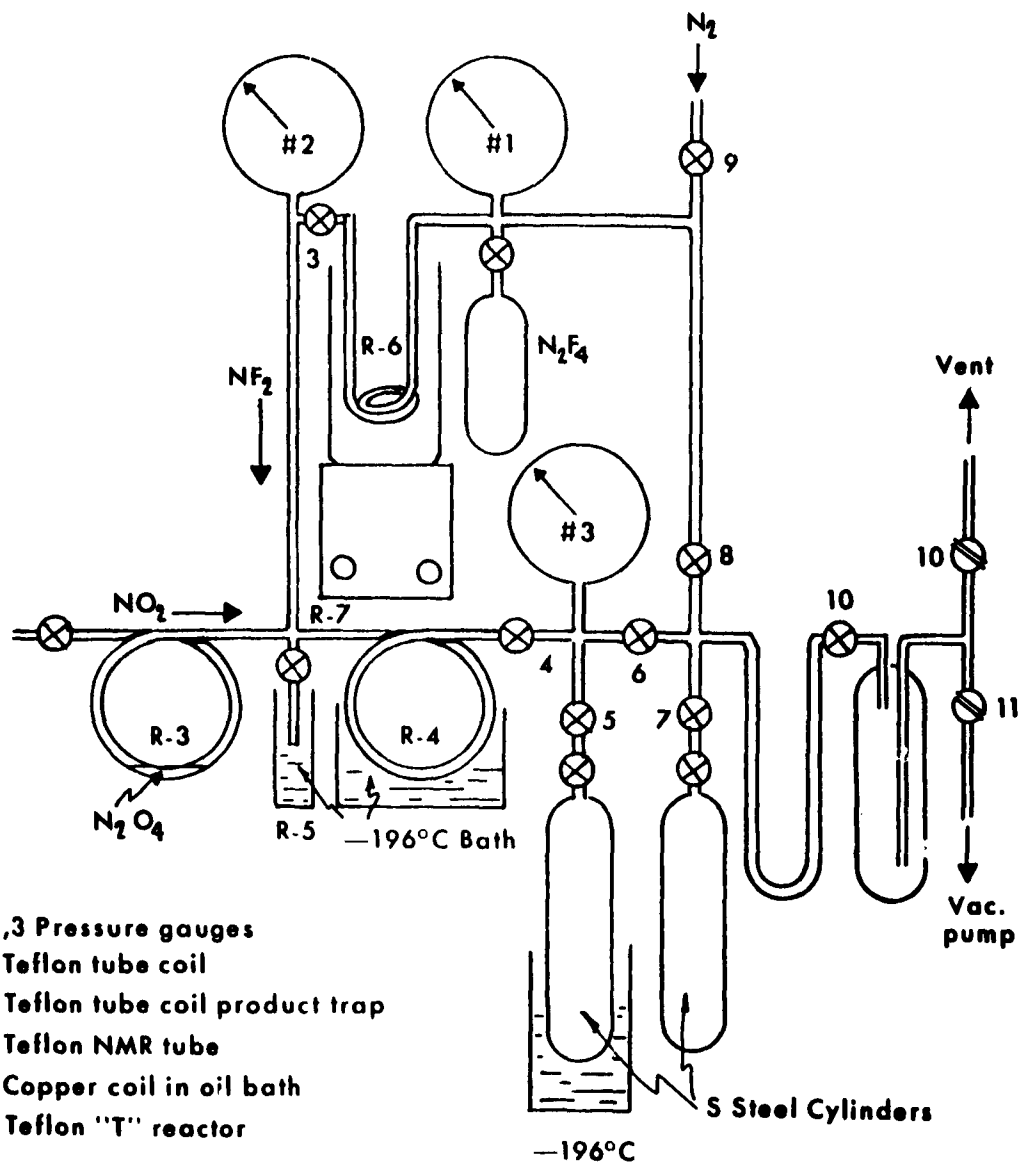
#1,2,3 Pressure gauges
R-3 Teflon tube coil
R-4 Teflon tube coil product trap
R-5 Teflon NMR tube
R-6 Copper coil in oil bath
R-7 Teflon "T" reactor

⊗ S Steel needle valves
⊘ Pyrex vacuum stopcocks

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At the completion of the experiment, the Teflon NMR tube still cooled to $-196°C$ was placed in the NMR instrument probe also precooled to $-196°C$ and the sample tube was slowly warmed to $25°C$ with constant scanning for fluorine signals to detect the presence of unstable N-F species.

The product that collected in the Teflon coil product trap R_4, was also fractionated and analyzed. In a typical experiment one gram of N_2O_4 was added to 2 grams or an excess of N_2F_4.

Results

The reaction of NO_2 with NF_2 radicals was investigated to study the low temperature decomposition of adducts of NF_2. It was hoped that information from this study would aid in the isolation of heretofore unknown derivatives such as NF_2NO_2, NF_2NO_3, and the like.

It was known that the reaction of N_2F_4 with N_2O_4 results in the formation of NF_3, NO and NOF (65)

$$2 N_2F_4 + N_2O_4 \longrightarrow 2 NOF + 2 NO + 2 NF_3$$

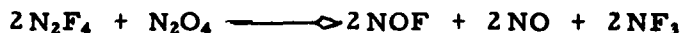but the decomposition reactions leading to these products were obscure. We have postulated that the reaction involves the following steps:

A. $NO_2\cdot + NF_2\cdot \longrightarrow \left[NF_2NO_2\right]$

B. $\left[NF_2NO_2\right] \longrightarrow 2 NOF$

C. $NOF + NF_2 + NO_2 \longrightarrow NF_3 + NO + NO_2$

$$NO_2 + 2 NF_2 \longrightarrow NF_3 + NO + NOF$$
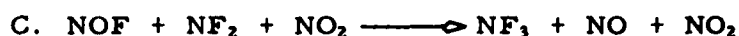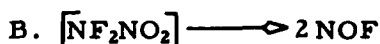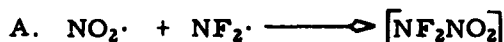
To confirm reaction A, a stream of NO_2 and excess NF_2 radicals was reacted in the apparatus described in Figure 43 and the products quenched directly into a Teflon NMR tube cooled to $-196°C$. The tube was placed in the NMR instrument probe, also precooled to $-196°C$, and then warmed slowly to $25°C$ with constant field scanning for fluorine signals. It was hoped that a fluorine signal could be detected for N-F bonding due to the presence of NF_2NO_2. Only N_2F_4 (chemical shift - 55 PPM relative to Freon-11) was detected. The low thermal conductivity of Teflon may have prevented the necessary rapid quenching of products to prevent decomposition. Further, the presence of excess N_2F_4 could have diluted the concentration of any NF_2NO_2, or its decomposition product NOF, and consequently only N_2F_4 signals were detected. Reaction A, therefore, was not confirmed.

To confirm reaction B, a special technique was employed which was based on the assumption that if the initial reaction of NO_2 with NF_2 radicals actually involves coupling and immediate decomposition to 2 moles of NOF, the reaction of NO_2 radicals with a large excess of NF_2 radicals

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would produce only a single product (NOF) provided NOF does not react with NF_2 radicals or N_2F_4.

As a preliminary step, a mixture of N_2F_4 and NOF was placed in a stainless steel 5-cm. infrared cell with silver chloride windows and scanned over a period of two hours. There was no evidence of a reaction. Finally the cell was heated to 200°C, and again there was no evidence of a reaction. The infrared spectra of the mixture of NOF and N_2F_4 before and after heating are shown in Figures 44 and 45. It was concluded that NF_3 is not formed by the following reaction

$$NOF + NF_2 \cdot \xrightarrow{\quad\quad} NF_3 + NO$$

and the reaction of NO_2 radicals with a large excess of NF_2 radicals should produce only NOF.

To confirm reaction B, N_2F_4 was placed in an infrared cell and a small cylinder containing N_2O_4 was attached to the cell. The apparatus was then placed on an Infracord spectrophotometer and scanned repeatedly while N_2O_4 was slowly diffused into the cell. Only NOF was detected as a product. There was no evidence for NF_3. The results are shown in Figure 46. On the basis of this evidence, it was postulated that NF_3 is formed by reaction C

$$NOF + NO_2 + NF_2 \xrightarrow{\quad\quad} NF_3 + NONO_2$$

and this should be demonstrable by the addition of N_2O_4 to a mixture of NOF and N_2F_4. When N_2O_4 was added to an infrared cell containing NOF and N_2F_4, an immediate reaction occurred and NF_3 was formed.

On the basis of this evidence, it was reasoned that while the diffusion of N_2O_4 into an excess of N_2F_4 produces only NOF, the reverse addition should produce only NF_3 and NO. When N_2F_4 actually was slowly diffused into a large excess of N_2O_4, only NF_3 and NO were detected. There was no evidence for NOF. The results are shown in Figure 47.

This combined data generally supports the formation of an unstable NF_2NO_2 and subsequent decomposition to NOF which, in turn, reacts with N_2F_4 in the presence of N_2O_4 to form NF_3 and NO.

1. $N_2F_4 + CH_4 + NF_2Cl$
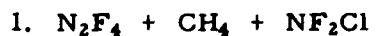
Material

N_2F_4. E.I. DuPont de Nemours and Company, purity 99%+

CH_4. The Matheson Company Inc., purity 99%+

NF_2Cl. Prepared by hypochlorination of NF_2H (Section X).

Apparatus

The apparatus is described in Figure 48. Material of construction

Figure 44

Gas mixture "A" (NOF + N₂F₄) after standing 2 hours at 25°C
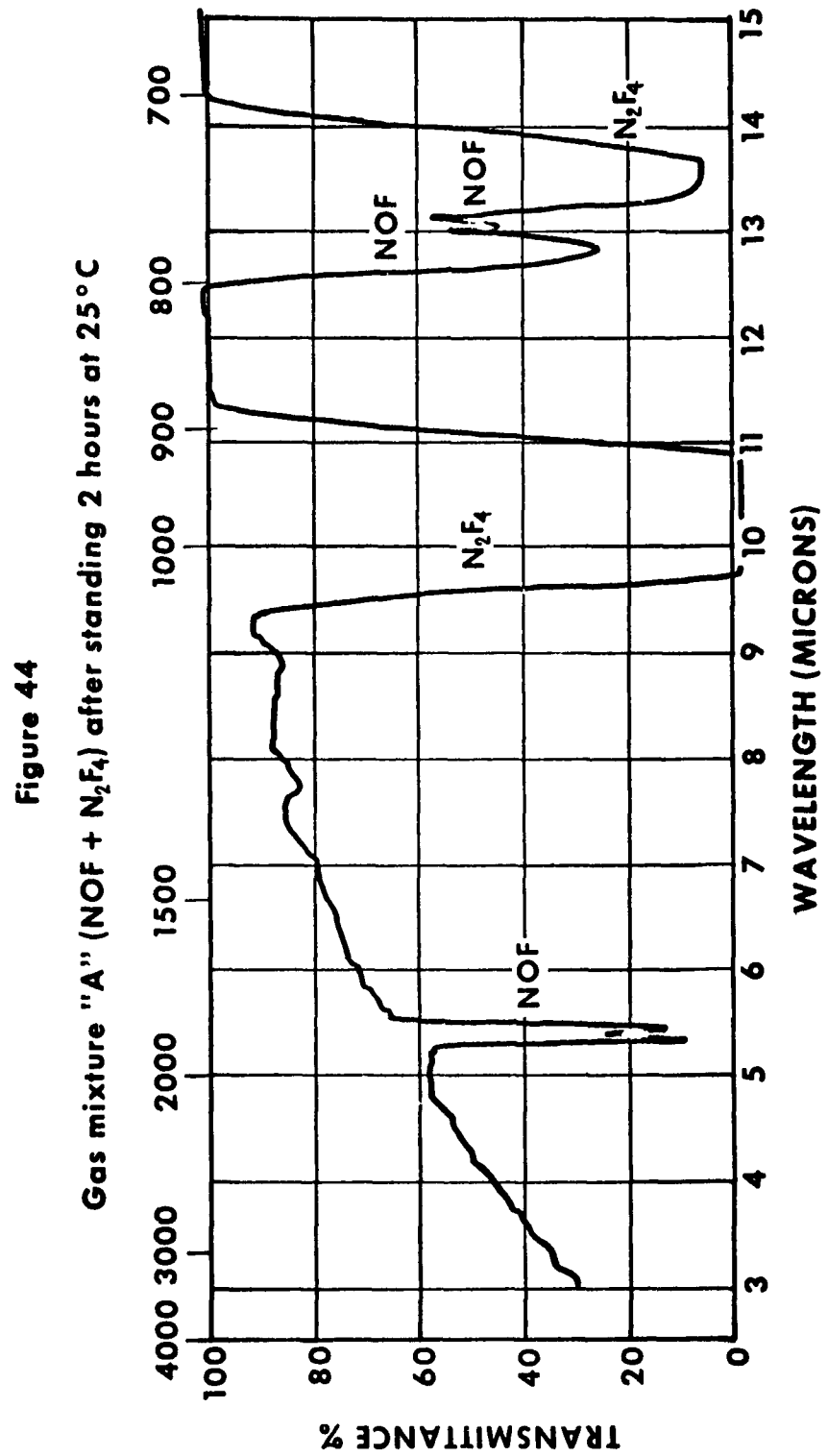
Figure 45

Gas mixture "A" (NOF + N₂F₄) after heating to 200°C in infrared cell

Figure 46

Slow diffusion of N_2O_4 into cell containing excess N_2F_4
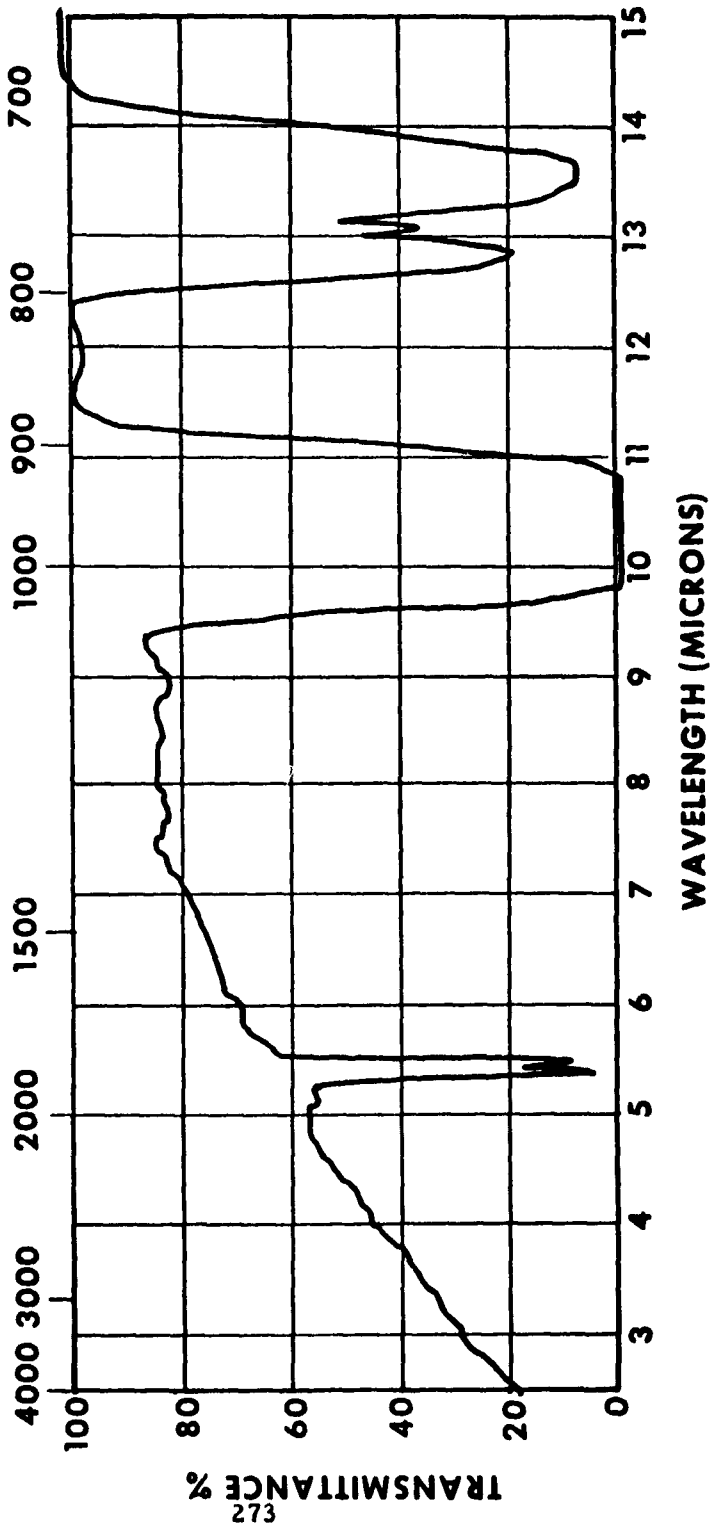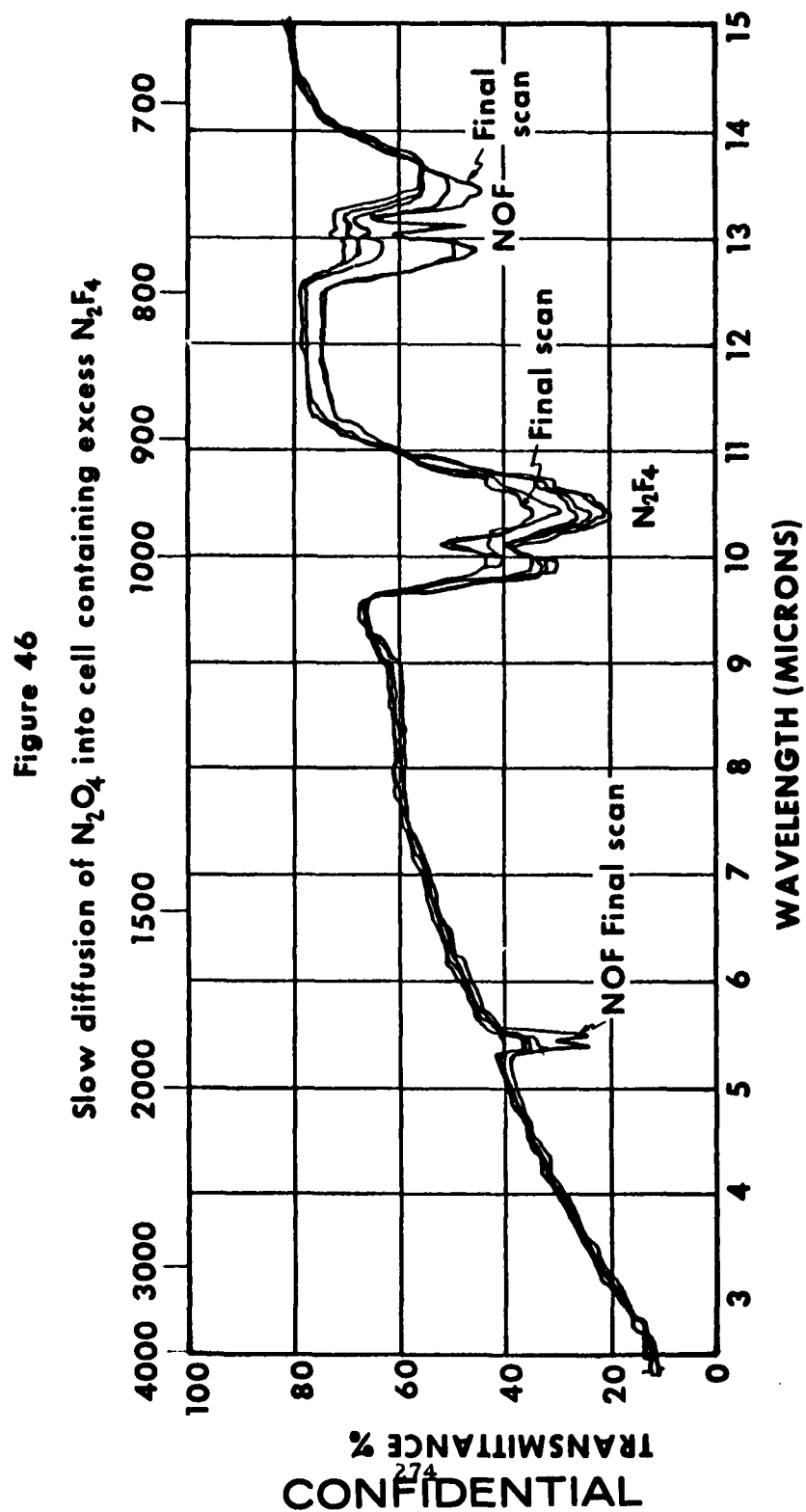
Figure 47

Slow diffusion of N_2F_4 to an infrared cell containing excess NO_2
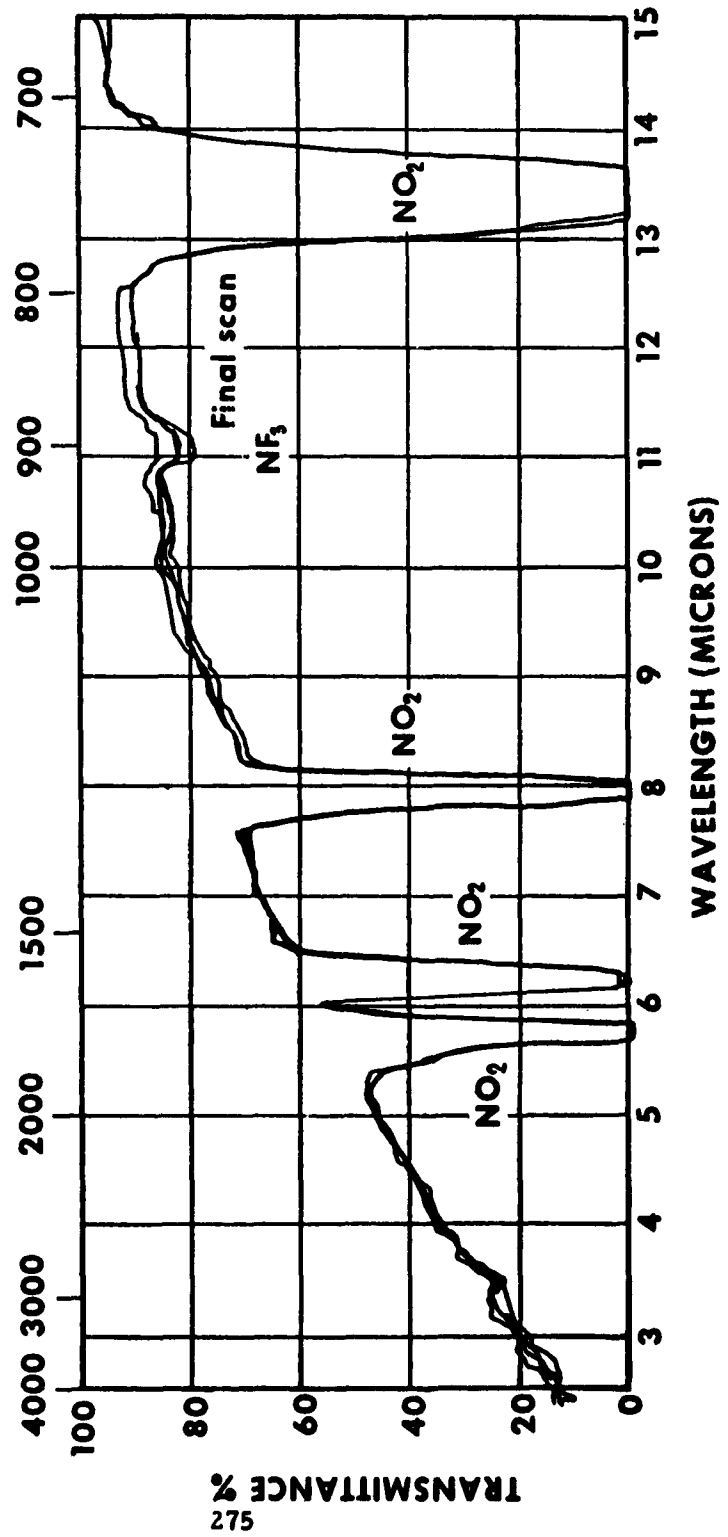
Figure 48

Irradiation Reactor System
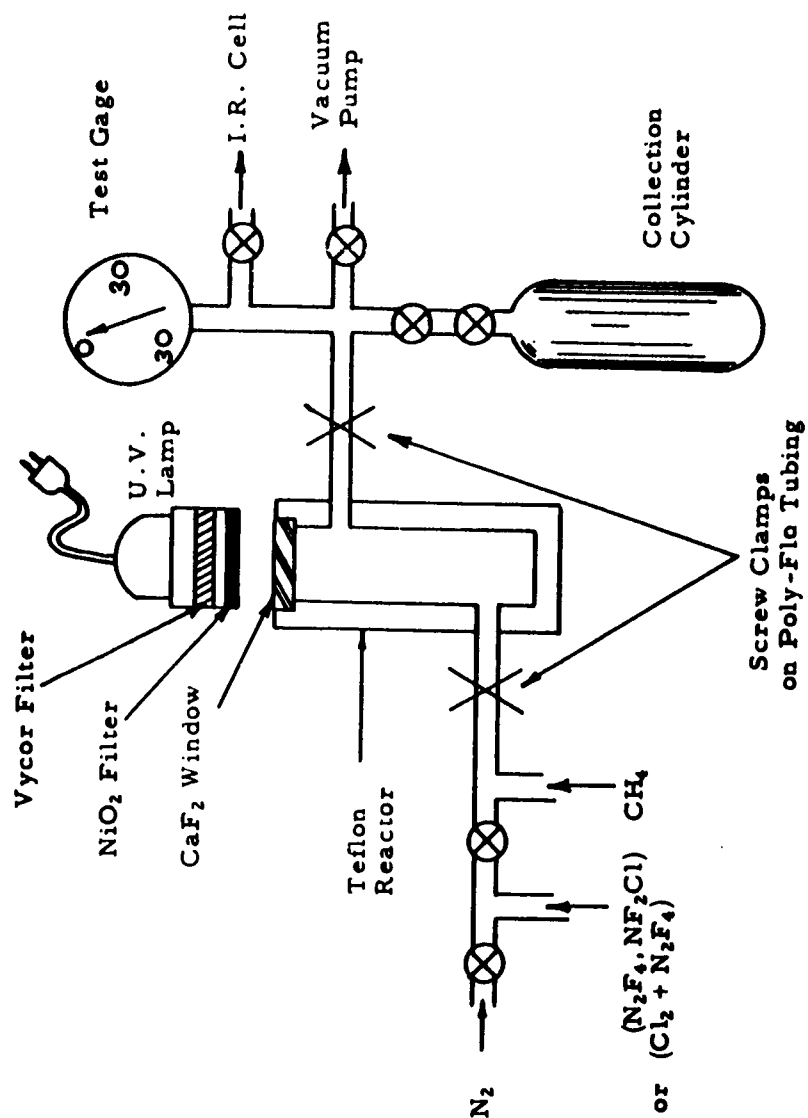
consisted of Teflon, polyethylene, copper tubing, and stainless steel.

Procedure

The general procedure adapted for this work is as follows: The entire system is evacuated and CH_4 introduced to a pressure of 300 mm. The mixture of N_2F_4 -NF_2Cl then is added in small portions until a total system pressure of 600 mm. is attained. The ultraviolet lamp then is turned on and the pressure and temperature recorded with time. At the end of 1.5 hours, a sample of the gaseous products is taken directly from the system for infrared examination and the remaining ga. .s condensed into a pre-cleaned stainless steel cylinder at -196°C.

The unreacted CH_4 is pumped off at -196°C and the remaining gases examined in the infrared. The N_2F_4 is removed from the products by pumping at -130°C. The infrared and mass spectra of the remaining gases then are recorded.

Results

The preparation of new oxidizers via photolysis reactions involving NF_2 radicals has not yet been successfully accomplished. Rohm and Haas investigated this approach both with chlorodifluoramine and with mixtures of chlorine and tetrafluorohydrazine. Although evidence was obtained for the formation of NF_2 derivatives, in general, the products decomposed under the reaction conditions. Our approach was intended to promote reactions under conditions where hydrogen abstraction by chlorine atoms preferentially occurs. This is then followed by a coupling reaction between the new radical and difluoramine radical.

$$NF_2Cl \xrightarrow{U.V.} NF_2 \cdot + Cl \cdot$$

$$Cl \cdot + RH \longrightarrow R \cdot + HCl$$

$$R \cdot + NF_2 \cdot \longrightarrow RNF_2$$
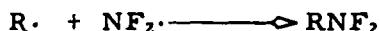
For the initial studies methane was employed as the RH source to gain a better understanding of the reaction variables important in the above scheme. The results of four experiments are summarized in Table 71.

It was demonstrated that, in the absence of ultraviolet irradiation, no reaction occurs between CH_4, N_2F_4, and NF_2Cl. With irradiation, the NF_2Cl disappears and a reaction occurs, as shown by the presence of CH_3Cl, CNCl, and CF- and NF- fragments. These products, which were collected at -130°C, constitute 20 per cent or less by weight of the total amount of gases. There seems to be little evidence for the presence of CH_3NF_2 other than trace amounts of NF-fragments in the mass spectrum. Differences among ultraviolet lamps did not seem to change the results markedly. The significance of the appearance of HCl has not been established since in many cases the mass spectrograph gives erroneous results for HCl in the presence of chlorine. The presence of CH_3Cl and CNCl

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Table 71

Irradiation Reactions

Experiment No.	Reactants	Reaction Time	Reaction Temp.	Pressure	Product Analysis
1801-90*	175 mm. CH_4 175 mm. N_2F_4-NF_2Cl	1 hr.	26°C up to 38°C	350 mm. up to 600 mm.	I.R. showed unreacted N_2F_4 and CH_4 and NOCl, but no NF_2Cl. Mass spectrum of -130°C fraction showed NOCl, N_2O, NO_2, CNCl, and CF and NF fragments.
1801-91**	300 mm. CH_4 300 mm. N_2F_4-NF_2Cl	1.5 hr	27°C up to 36°C	600 mm. up to 625 mm.	I.R. showed unreacted N_2F_4 and CH_4 and NOCl, but no NF_2Cl. Mass spectrum of -130°C fraction showed CH_3Cl and smaller amounts of NO_2, NO, N_2O, CNCl and NF and CF fragments.
1801-92***	300 mm. CH_4 300 mm. N_2F_4-NF_2Cl	1.5 hr.	27°C up to 28°C	constant 600 mm.	I.R. showed unreacted N_2F_4, NF_2Cl, and CH_4. N.R.
1801-93**	300 mm. CH_4 237 mm. N_2F_4 63 mm. Cl_2	1.5 hr.	27°C up to 34°C	600 mm. up to 650 mm.	I.R. showed unreacted N_2F_4 and CH_4 and NOCl. Mass spectrum of -130°C fraction shows NOCl, HCl, Cl_2, CNCl and possible CH_3Cl and N-F fragments.

* Sargent B-100A Blak-Ray U.V. Lamp Purple heat filter gives 3660 Å max.

** Hanovia No. 30600 U.V. Lamp Vycor + NiO_2 filter gives 2500-3700 Å max.

*** No U.V. Irradiation used.

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suggests that the following reactions may be occurring:

$$NF_2Cl \xrightarrow{\text{U.V.}} NF_2 \cdot + Cl \cdot$$

$$CH_4 + Cl \cdot \longrightarrow CH_3 \cdot + HCl$$

$$CH_3 \cdot + Cl \cdot \longrightarrow CH_3Cl$$

$$CH_3 \cdot + NF_2 \cdot \longrightarrow (CH_3NF_2) \longrightarrow HCN + 2HF$$

$$HCN + Cl \cdot \longrightarrow HCl + CN \cdot$$

$$CN \cdot + Cl \cdot \longrightarrow CNCl$$
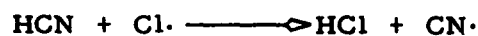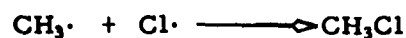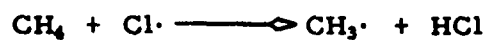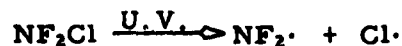
Mass spectral data on the last reaction involving CH_4-N_2F_4-Cl_2 (No. 1801-93) does show evidence for NOCl, HCl, Cl_2, CNCl, and CH_3Cl. This material constitutes about 10 per cent of the total amount of gaseous products involved in the reaction. The appearance of HCl is encouraging and supports the postulated theory.

On the basis of this preliminary study, it could not be confirmed that chlorine atoms generated by ultraviolet activation of NF_2Cl, or chlorine, will abstract a hydrogen from methane to liberate an alkyl radical to react with NF_2 radicals.

B. Reactions with NF_2Cl

1. Objective

The primary objective of the study of reactions with NF_2Cl was to prepare new solid oxidizers such as NF_2ClO_3, NF_2ClO_4 and/or new intermediates which could be used to prepare these compounds. A secondary objective was to elucidate the chemical behavior of NF_2Cl so that selection of synthesis methods for the preparation of the desired compounds could be based on firm experimental data rather than on analogies.

In the initial selection of reactions to be investigated, the structure and polarization of NF_2Cl were considered. Chlorodifluoramine is expected to be polarized so that the chlorine is positive with respect to the difluoramine group,

$$\overset{\delta+}{Cl} \quad - \quad \overset{\delta-}{NF_2};$$

the electronegativity value for chlorine being 3.0 (73) as compared to a value of 3.26 for NF_2 (74). Similarly, in $ClNO_2$, the nitro group has an electronegativity value of 3.45 (75), indicating that reactions here also would be expected to occur by displacement of chlorine as a positive substituent. However, in some cases the influence of the attacking reagent will result in elimination of chlorine as the negative ion. Schmeisser (76, 77) has suggested that the chemical properties of nitryl chloride can best be explained by a resonance polarization in which either the chlorine or nitro substituent is positive.

$$\overset{\delta+}{NO_2} - \overset{\delta-}{Cl} \Longleftrightarrow \overset{\delta+}{Cl} - \overset{\delta-}{NO_2}$$
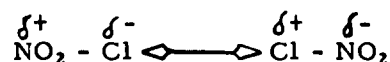
Similarly, the properties of chlorodifluoramine perhaps may be appropriately designated as being due to a similar polarization.

$$\overset{+}{NF_2} - \overset{-}{Cl} \Longleftrightarrow \overset{+}{Cl} - \overset{-}{NF_2}$$

Previous work had shown that the reactions of silver chlorate and silver perchlorate with chlorodifluoramine resulted in the precipitation of silver chloride (67, 68).

$$Ag\,X + ClNF_2 \longrightarrow AgCl\downarrow + [?]$$

The displacement of chlorine as the negative component from $ClNF_2$ suggested that attempts to prepare compounds in which the difluoramine group would exist as the cation might be a promising approach to a new oxidizer.

In the experimental section that follows, unless otherwise stated, the NF_2Cl was prepared by the reaction of NF_2H with aqueous $NaOCl$, as described in Section X of this report.

a. NF₂Cl + AgClO₃

$$\text{a. } NF_2Cl + AgClO_3$$

Material

AgClO₃. Prepared by the method of Holley and Nicholson (64) by the following reaction:

$$AgNO_3 + NaClO_3 \longrightarrow NaNO_3 + AgClO_3$$
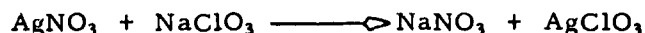
Apparatus

The apparatus, as described in Figure 49, was constructed of Pyrex glass.

Procedure

In a typical experiment, 1.5 g. of gaseous NF₂Cl was passed through a solution consisting of 2 g. of AgClO₃ in 50 ml. of water until a pressure of 200 mm. developed in the system. The gaseous products were then pumped through fractionating cold traps. This addition of NF₂Cl to the aqueous solution was repeated 3 to 5 times.

Results

In an attempt to elucidate the chemical behavior of NF₂Cl in polar solvents such as water, the reaction of NF₂Cl with AgClO₃ was chosen for study. The objective was to prepare NF₂ClO₃, according to the following equation,

$$AgClO_3 + NF_2Cl \xrightarrow{\text{H}_2\text{O}} NF_2ClO_3 + AgCl\downarrow$$
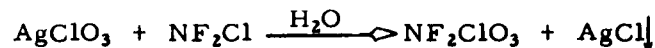
The desirable aspect of using water as a solvent is the insolubility of the silver chloride, but the possible hydrolysis of NF₂ClO₃, if it forms, is not to be overlooked. Since NF₂Cl, NF₂H and N₂F₄ do not undergo rapid hydrolysis it was hoped that NF₂ClO₃ might exhibit similar hydrolytic stability.

The results of this investigation are summarized in Table 72.

When the NF₂Cl was first introduced, a precipitate formed immediately. After several minutes, a sudden pressure increase occurred, followed by a decrease and the simultaneous formation of a second precipitate. Silver chloride was definitely identified in the solid product but no nitrogen could be found and only traces of fluorine could be detected. The gaseous products showed high concentrations of nitrogen oxides and lesser concentrations of NF₃, NOCl, and SiF₄. All the NF₂Cl had reacted. There was no evidence for the formation of NF₂ClO₃ or any other new N-F product.

The formation of AgCl and the observed physical changes, however, prompted an investigation of this reaction in the absence of water.

In the solid-gas reaction of silver chlorate with NF₂Cl, a yellow solid

Figure 49

Reaction System: $NF_2Cl - AgClO_3$

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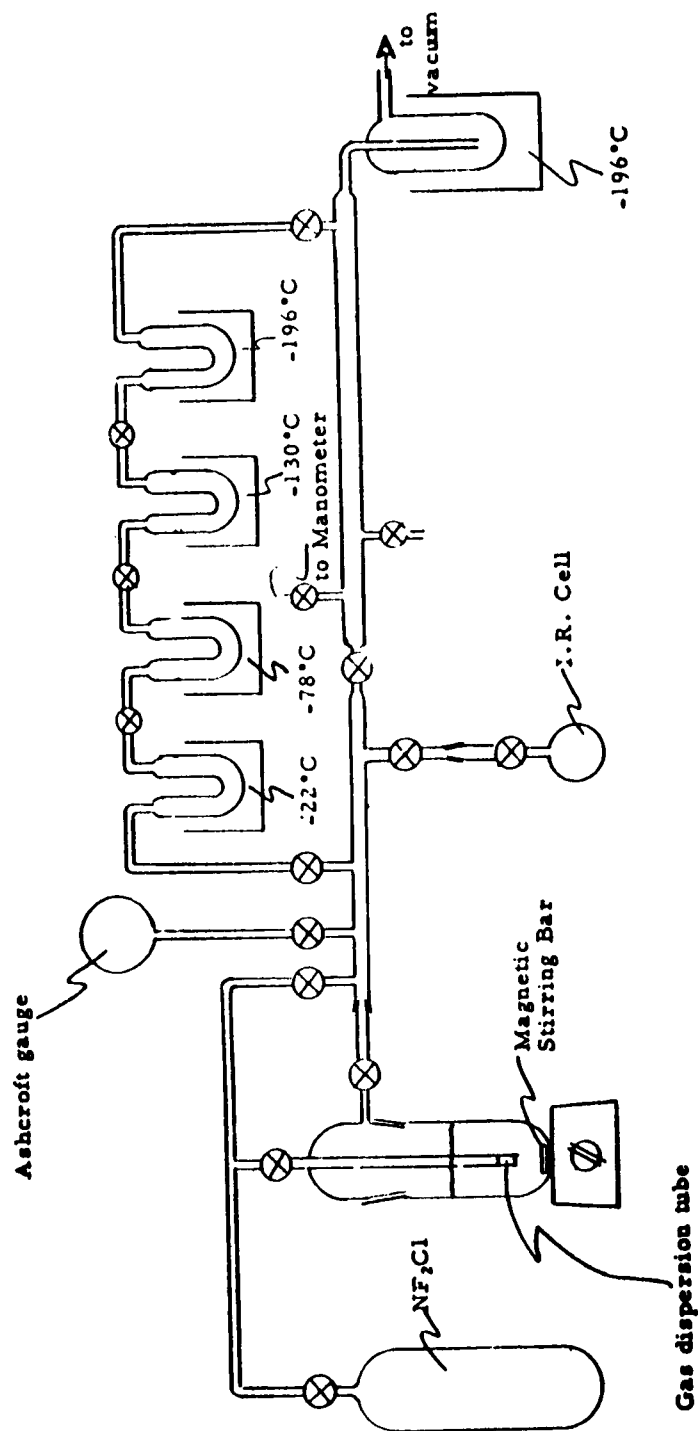
Table 72

Reaction of NF_2Cl with $AgClO_3$

Expt. No.	Reactants (g.) NF₂Cl	AgClO₃	H₂O (g.)	Reactor T°C	Solid Product Infrared	X-ray	Element%	Gaseous Product Infrared	Water Solution Infrared
2339D-15	Cal	Excess	40	25	$AgClO_3$	$AgClO_3$, AgCl	N=0	NOCl NO₂	-
2339D-21	1.6	1.8	50	25	No absorption bands	AgCl	Ag=52.5 Cl=3.7 F=0.7 N=0	NOCl NO₂ SiF₄	NO₃⁻ NO₂⁻
2339D-24	1.6	1.9	50	25	Unidentified absorption band at 9-10 microns	AgCl	Ag=69.2 Cl=23.8 F=0.1 N=0	NOCl NO N₂O NF₃	NO₃⁻
2339D-25	1.5 (approx.)	2	-	25	strong unidentified bands at 11 microns	$AgClO_3$	Ag=61 Cl=12.5 F=1.0 N=2.3	HNO₃ ClO₂ N₂O NF₂Cl	-

was formed, which rapidly decomposed on exposure to light and/or air. The partially decomposed solid contained unreacted $AgClO_3$ and unidentified components.

The reaction of NF_2Cl and $AgClO_3$ resulted in the formation of AgCl, an expected product, but the desired compound NF_2ClO_3 was not detected.

(b) $NF_2Cl + HClO_4$
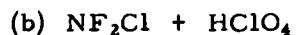
Material

$HClO_4$. Prepared by the reaction of aqueous $HClO_4$ and fuming H_2SO_4 by the method of Smith (62). A detailed procedure is given in Section VI A-1, g).

Apparatus

The reactor consisted of a one-liter Teflon vessel which is described in Figure 15. This reactor was attached to a typical general purpose material transfer line.

Procedure

In a typical experiment, 1-2 grams of anhydrous perchloric acid was dissolved in 30 ml. of carbon tetrachloride. The carbon tetrachloride solution was placed in the Teflon reactor, the reactor pressured with approximately 1 gram of NF_2Cl, and the reactants held at 25°C. for 18 hours. The products were then fractionated and analyzed.

Results

The reaction of NF_2Cl with anhydrous $HClO_4$ was investigated as a possible route to NF_2ClO_4:

$$NF_2Cl + HClO_4 \longrightarrow NF_2ClO_4 + HCl$$
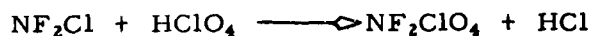
The results are summarized in Table 73. A complex reaction occurred to produce a large number of decomposition products; NO_2, ClO_2, N_2O, HNO_3, NOCl and solid $NOClO_4$.

The absence of HCl in the products, coupled with the formation of nitrogen oxides, indicated that the proposed reaction did not take place. The fluorine may have remained dissolved in the carbon tetrachloride solution as HF, although it was not detected by infrared analysis.

(c) $NF_2Cl + LiClO_4$
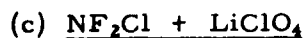
Material

NF_2Cl. Prepared by the reaction of BCl_3 with NF_2H, as described by Petry (69).

$LiClO_4$. American Potash and Chemical Corporation

Table 73

Reaction of NF_2Cl with $HClO_4$

Expt. No.	Wt. $HClO_4$ (g.)	Wt. NF_2Cl (g.)	Vol. CCl_4 (cc.)	Time (hrs.)	Wt. Solids (g.)	I. R. Analysis		Elemental Analysis	X-ray Diffraction
						CCl_4 Soln.	Product Gases		
2375D-17	2.0 10% Soln. of Anhyd. $HClO_4$ in CCl_4	1.5	30	18	0.8892	NF_2Cl $HClO_4$ NO_2 $NOCl$	NF_2Cl NO_2, N_2O HNO_3 $HClO_4$ ClO_2 CCl_4	%F=0 %Cl=25.51 %N=14.99	$NOClO_4$
2375D-20	1.0	0.43	30	68	0.028	$HClO_4$	NF_2Cl $NOCl$ SiF_4	%F=trace	

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Apparatus

The Pyrex glass apparatus is described in Figure 50.

Procedure

In a typical experiment 3 g. of $LiClO_4$ was placed in the reactor. About 20 ml. of solvent (either CCl_4, CH_3OH, $(CH_3)_2S=O$) was then added to give either a solution or a slurry, depending on the solvent used. The chlorodifluoroamine was bubbled through the solution and chlorodifluoroamine pressure was held over the solution for 18 hrs. at 25°C. while the solution was stirred. The solvent was then distilled off and the volatile and solid products were analyzed.

Results

Reaction in solution was sought because both ionic and free radical mechanisms can take place depending on the nature of the solvents. Further, the use of a solvent was considered to be advantageous in quickly distributing the heat in exothermic reactions.

The objective of this study was to prepare the compound NF_2ClO_4 by the following reaction:

$$NF_2Cl + LiClO_4 \xrightarrow{\text{Solvent}} NF_2ClO_4 + LiCl$$
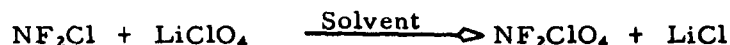
The results of several experiments are summarized in Table 74.

In all experiments the chlorodifluoroamine reacted to give tetrafluoro-hydrazine as the major volatile product. A solid product was also recovered in each case and the amount of fluorine in the solid increased with increasing solubility of the chlorodifluoroamine in the solvent. In the reaction with methanol as a solvent, the solid product contained 8.4 per cent fluorine. This solid probably contained unreacted lithium perchlorate as well as some fluorine containing components, possibly HF adducted to $LiClO_4$. The nature of the fluorine bonding in the products was not resolved. However, the formation of N_2F_4 was not encouraging since this indicated that NF_2 groups were not reacting to form the desired NF_2ClO_4.

(d) $NF_2Cl + NO_2 SbF_6$

Material

NO_2SbF_6. Prepared by the method of Kuhn and Olah(71).

SbF_5 was dissolved in Freon-11 and an excess of nitrosy fluoride bubbled through the solution cooled to 0°C. The solid that precipitated was washed with Freon-11, and then dried under vacuum for 24 hours.

Figure 50

Apparatus for Reaction of Chlorodifluoramine with Perchlorates
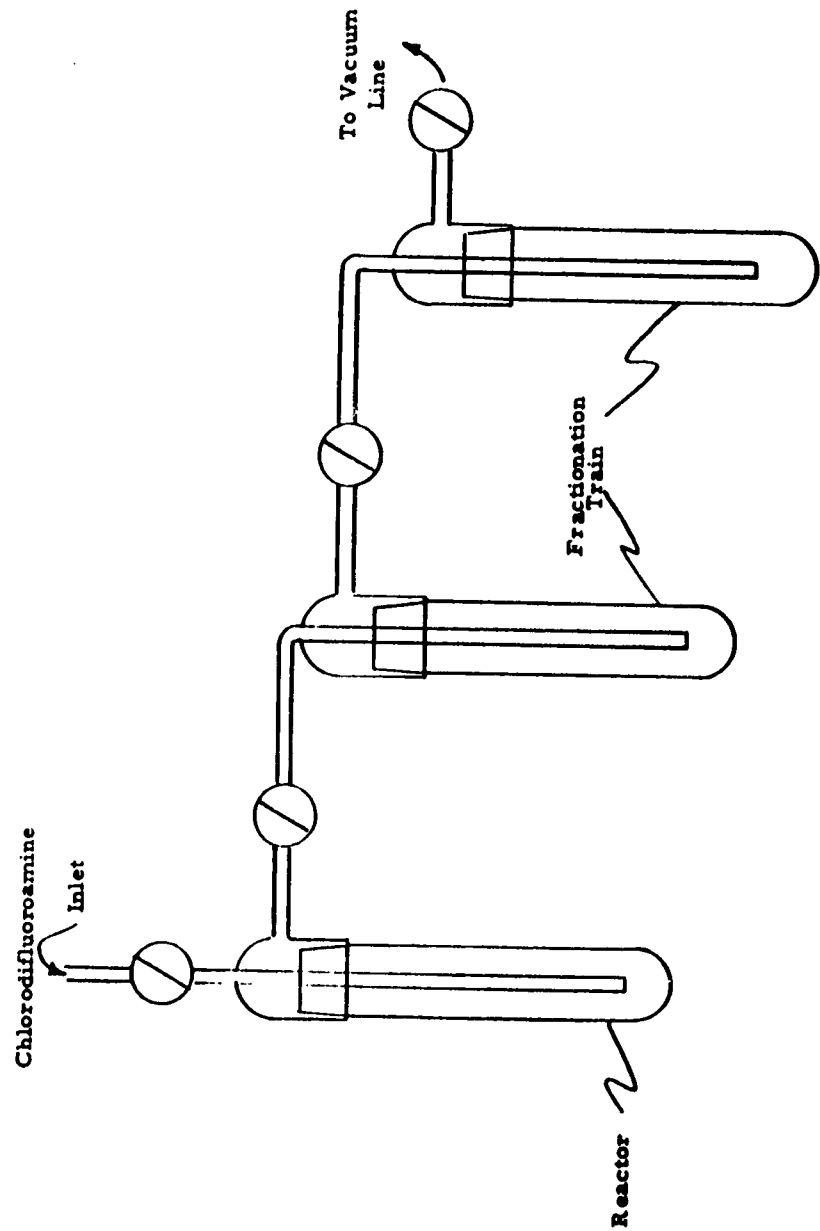
Table 74

Reactions of Difluorochloroamine with Perchlorates

Experiment No.	Weight of Reactants (g.)		Solvent (ml)	Temp. (°C.)	Time of Reaction (Hours)	Volatile Products	Elemental Analysis of Solid Products (%)	Comments
18100-92	NF_2Cl 0.5	$LiClO_4$ 3.62	CCl_4 10	25	18	N_2F_4, N_2O NF_2Cl	Li 4.8, Cl 29.9, F 3.6, N 0.15	Theoretical for $LiClO_4$: Li 6.5, Cl 33.4
1810D-95	NF_2Cl 0.6	$LiClO_4$ 3.44	$(CH_3)_2S{=}O$ 1.5	25	2	N_2F_4, small amounts of Nitrogen oxides. No NF_2Cl.	Contained no fluorine	After one-half of the solvent was removed; remaining material solidified.
1810D-97	NF_2Cl 0.4	NH_4ClO_4 0.927	CH_3OH 20	25	3	No NF_2Cl, small amount N_2F_4	N 9.39, No fluorine, Cl 24.9	
1810D-99	NF_2Cl 0.5	$LiClO_4$ 1.763	C_2H_5OH 20	25 50	2.5 0.5	No NF_2Cl Some N_2F_4	F 8.4	
1810D-102	NF_2Cl 0.6	$LiClO_4$ 3.701	CCl_4 25	25	5	NF_2Cl, N_2F_4 N_2O	F 3.7	

Analysis of the solid NO_2SbF_6 showed,

		Found	Theoretical for NO_2SbF_6
Wt%	F	40.7	40.5
	N	6.0	5.0
	Sb	41.0	43.2

Apparatus

The apparatus is described in Figure 51.

The reactor consisted of a Teflon tube coil R_1 which was attached to a copper high vacuum line equipped with pressure gauge.

Procedure

In a typical experiment the apparatus was evacuated, filled with high purity dry nitrogen gas and 0.13 g. of NO_2SbF_6 placed in the reactor R_1. The nitrogen gas was then pumped out and 0.714 g. of NF_2Cl condensed into the reactor. The reactor was then isolated from all metal parts by collapsing the tube between R_1 and R_2 with a tube clamp. The reactants stood for 67 hours at -78°C. The products were then fractionated and analyzed.

Results

The reaction shown below was investigated after several exploratory experiments had been conducted in a stainless steel bomb at a temperature of -130°C.

$$NO_2SbF_6 + NF_2Cl \longrightarrow NF_2SbF_6 + NO_2Cl$$

In these initial experiments, conversion of all the NF_2Cl was observed, with the isolation of a solid whose elemental composition corresponded to that for NF_2SbF_6.

		Found	Theoretical for NF_2SbF_6	Theoretical for NO_2SbF_6
Wt%	F	52.7	52.8	40.0
	N	4.4	4.9	5.0

Infrared analysis of the solid dispersed in Nujol, however, showed that the spectra of the recovered solid product and that of the starting NO_2SbF_6 were identical. Additional experiments were conducted in the metal system and in each case the NF_2Cl was converted and the recovered solid product appeared to be unreacted NO_6SbF_6. These results are summarized in Table 75, Experiments 5001-29, 41, and 44. The decomposition of NF_2Cl was believed to be catalyzed by the metal system rather than by reaction with NO_2SbF_6.

Finally, the reaction was investigated in the all Teflon system described in Figure 51.

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Figure 51: Teflon Apparatus for Reactions of NF_2Cl

#1, #2 Helicoid Press - Vac. Gage
#3 Ashcroft Press - Vac. Gage
A 175 ml S. Steel Cyl.
C NF_2Cl Cyl.
E Cold bath or Ultrasonic Cleaning Tank
D Cold bath -196°C or -78°C
R_1 Teflon Tubing Containing Solid Reactant
R_2 Teflon Tubing
B I R Cell

═══ Teflon Tubing
≡≡≡ Copper Tubing
▭▭▭ Pyrex Tubing
⊗ ¼" S. Steel Needle Valve
Ø Pyrex Vac. Stopcock
✕ Fisher Tubing Clamps
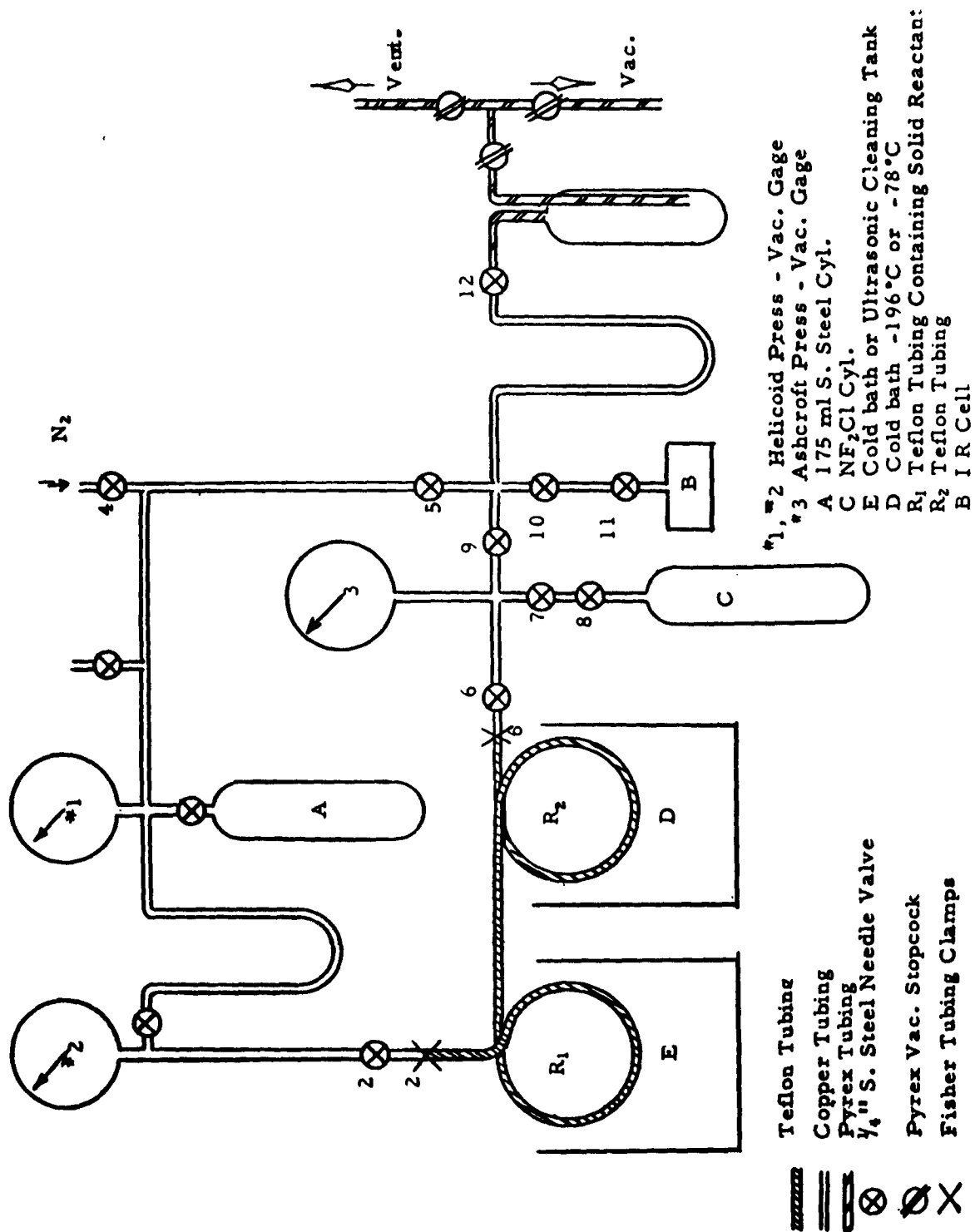
Table 75

Reaction of NO₂SbF₆ with NF₂Cl

Experiment No.	Reactants			Cond.	Products Recovered		Product Anal					
	Cmple	Amt.	Anal.		Solid	Gas	Solid I.R.	X-ray	NMR	Gases I.R.	M.S.	mole %
5001-33	XBF₄	1.119g	%F 56, N 9.7%, B 9.2%	Teflon tube in as reactor ambient temp. at approx. 20 hrs. with stirring	1.032g	0.626g	F 59.8, 58.9%, N 10.8, 10.02%, B 10.6, 11.2% Absorptions indicate NO_2BF_4	NO_2BF_4	MeNO₂ sh. BF_4 (tetramethylene sulfone) BF_4	NOCl, N₂O, NO₂	N₂, NOCl, N₂O, HCl	52.2, 25.6, 9.5, 12.5
	NF₂Cl	1.422g	97% N_2F_4									
5001-33A, 5001-33B	See text for description of decomposition results.											
5001-39	NO₂SbF₆	2.341	F 41.0% N 3.86%	Teflon tube in as reactor ambient temp. for 22 hrs. with stirring	2.322 g		F 41.8, 40g N 4.61	6.0 , 7.6 7.8 abs. disappear no new peak		N₂O, NOCl, NO₂	N₂, NOCl, N₂O	22.9, 65.1, 12.0
	NF₂Cl	0.980g	92% NF_2Cl, 8% N_2F_4			0.257g						
5001-41	NO₂SbF₆	2.533	See above	Teflon tube in as reactor -46°-20°C for 5 hrs with stirring; NOCl solvent	2.632g	3.411g. (includes NOCl)	F 40.0, 39.2% N 4.60%, 4.85%% Same as Expt.-39		N₂O, NOF, NO₂, N_2F_4	N₂O, NOF, N_2F_4, SiF₄	2.5, 86.3, 10.7, 0.5
	NF₂Cl	1.345	97% NF_2Cl, 3% N_2F_4									
5001-44	NO₂SbF₆	1.361	See 5001-39	All Teflon reactor, -46-20°C for 5-1/2 hrs, with stirring. NOCl solvent	1.241g	0.540g	%F 40.40, 41.02 Same as %N 4.66 -39			NF₂Cl, N_2F_4, N₂O, NOCl, N₂	9.2, 48.6, 1.6, 9.0, 17.4
	NF₂Cl	1.240	Same as -41									

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In the Teflon reactor, there was no evidence of a reaction or decomposition of the NF_2Cl. The infrared spectrum of the recovered NF_2Cl was identical to that of the starting NF_2Cl and analysis of the recovered solid showed no significant change in fluorine content over that of the starting NO_2SBF_6:

		Starting NO_2SbF_6	Recovered Solid	Theoretical for NO_2SbF_6	NF_2SbF_6
W %	F	40.7	38.6	40.5	52.8
	N	6.0	7.1	5.0	4.9

A material balance on the reactants showed 82.5% NF_2Cl recovered and 81.4% NO_2SbF_6 recovered. The low material balance was attributed to handling losses since the amount of reactants involved was small.

It was concluded that there is no reaction between NO_2SbF_6 and NF_2Cl at -78°C. in an all Teflon system. Results are summarized in Table 76.

(e) NF_2Cl + $NOBF_4$

Material

$NOBF_4$. Nitrosyl fluoroborate was prepared by the reaction of nitrosyl fluoride with boron trifluoride. The infrared spectrum of the solid product was identical to that published by Sprague, Garrett, and Sisler (70).

Analysis showed:

		Found	Theory for $NOBF_4$
Wt%	F	63.3	64.9
	N	14.9	12.0

Apparatus

This reaction was investigated in two basic systems. In the first, the reactor constructed of either stainless steel, Pyrex glass, or Kel-F, (approximately 200 ml. volume) was attached to a general purpose metal high vacuum line equipped with a pressure guage.

The second apparatus consisted of the Teflon reactor R_1 with supporting equipment as described in Figure 51.

Procedure

(Stainless Steel Reactor)

In a typical procedure the reactor (glass, stainless steel, or stainless steel with a Teflon or polyethylene insert), is attached to a metal vacuum line after a weighed amount of salt has been placed in the reactor. The system is evacuated, cooled to -196°C. and weighed amounts of solvent (when used) and chlorodifluoramine are added. The mixture then is

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Table 76

Reaction of NF$_2$Cl with NO$_2$SbF$_6$

Experiment No.   1891-55

I Reactants

      NO$_2$SbF$_6$ 0.130 g.

      NF$_2$Cl   0.714 g.

                                       0.844 g.

II Experiment Conditions

      Reactor Type   Teflon

      Reaction Time   67 hrs.

      T°C.   -78

III Products

      Solid   0.106 g.

      Gaseous   0.589 g.

                                     .695 g.

IV % Material Recovered   82.3

V Product Analysis			Found	Theoretical for NF$_2$SbF$_6$	NO$_2$SbF$_6$
Solid	wt. %	F	38.6	52.8	40.5
		N	7.1	4.9	5.0

      Gaseous   Infrared spectrum was identical to NF$_2$Cl

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permitted to stand with stirring for a specified time and at a predetermined temperature. At the end of the reaction period the effluent gases are condensed, weighed and analyzed. The reactor containing the solid is pressured to slightly greater than atmospheric pressure, opened in a dry box and the solid is collected for analysis.

(Teflon Reactor)

In a typical experiment the Teflon tubing, after being dried and checked for leaks, is charged with the solid reactant in a nitrogen dry box and then attached as shown in Figure 51. The coils R_1 and R_2 are evacuated through clamp 6 and valve 6. A bath at -78°C. is placed around R_2. A known quantity of chlorodifluoramine is distilled into R_1 and clamp 6 and valve 6 are closed. The reactants now are completely isolated from all materials of construction except Teflon. The bath at -196°C. is removed from R_1 and the Teflon reactor coil is warmed at 25°C. The reactants are maintained together for the desired time before the gases are removed and the components analyzed. In some experiments R_1 was agitated with an ultrasonic generator, National Ultrasonic Corp., Model G220.

Chorodifluoramine exerts a vapor pressure of approximately 400 mm. at -78°C. so that a constant pressure of NF_2Cl was in contact with the solid in R_1. After the reaction is terminated the gaseous products are condensed into cylinder C, weighed, and analyzed. The solid product is removed from R_1, weighed, and analyzed.

Results

The results of experiments conducted in the apparatus which utilized either a stainless steel or a Pyrex reactor are summarized in Tables 77, 78, and 79.

The reaction of nitrosyl tetrafluoroborate with chlorodifluoramine was investigated rather extensively when the results of preliminary experiments indicated that the following reaction may have taken place:

$$NOBF_4 + NF_2Cl \longrightarrow NF_2BF_4 + NOCl$$

In every case, the chlorodifluoramine either disappeared completely or its concentration in the recovered gases decreased markedly. Furthermore, in every case, nitrosyl chloride was formed. In several of the experiments the starting NF_2Cl was contaminated with NOCl; in these cases a large increase in the NOCl concentration in the product gases was observed. The elemental compositions of the products were very encouraging in some cases but poor in others. The theoretical fluorine content in NF_2BF_4 is 82.0%. In Experiment 57, Table 79, a value of 84.3% was obtained; in Experiment 63, Table 79, reproducibility was extremely poor but one of the values was 81.1%. There are no known solid materials whose fluorine contents would fall in this region. Nitrosyl tetrafluoroborate has a fluorine content of 64.9 per cent. Although complexes of hydrogen fluoride with $NOBF_4$ have not been reported these would be the only products whose fluorine values could approach the 80 per cent level, as shown on the following page.

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Table 77

Reaction of NOBF$_4$ with NF$_2$Cl

Experiment No.	Reactants Used NOBF$_4$	Reactants Used NF$_2$Cl	Reactants Recovered Solid	Reactants Recovered Gas	Reactor Type	Experimental Conditions	Product Analysis Solid	Product Analysis Gases	Comments
1891-89	0.590	2.261	.750	2.176	Pyrex glass	18 hrs, -78°C	IR: NOBF$_4$ X-ray: NOBF$_4$	IR: NF$_2$Cl	No reaction
1891-94	0.338	0.372	0.387	0.129	Pyrex glass open to metal gauge	65 hrs, R.T.	IR: NOBF$_4$; X-ray: NOBF$_4$ Elem. Anal: %F, 62.5, 61.7 %N, 11.28, 11.03	IR: N$_2$O, NOCl, NO, SiF$_4$	NF$_2$Cl completely consumed. NOBF$_4$ recovered unchanged.
1891-98	1.975	1.774	2.059	1.374	Pyrex glass open to metal gauge	18 hrs., R.T.	IR: NOBF$_4$;x-ray: NOBF$_4$	IR:NOCl, SiF$_4$, NF$_2$Cl, N$_2$F$_4$, N$_2$O	NOBF$_4$ recovered unchanged.
1943-03	0.585	0.559	0.597	--	Teflon tube	67 hrs. R.T. solvent acetonitrile (7.8 gm)	IR:NOBF$_4$;x-ray: NOBF$_4$ Elem.Anal: %F, 53.0, 54.2 %N, 8.43 NMR of acetonitrile solution showed only B-F type fluorine	IR:NOCl, N$_2$F$_4$,N$_2$O, NO,NOF	NOBF$_4$ recovered unchanged. NF$_2$Cl completely consumed.
9001-19A	2.2706	1.912	2.4558	1.645	Teflon insert in stainless steel	2 hrs, -130°C 10 hrs, R.T.	IR: NOBF$_4$	IR: No change-No reaction NF$_2$Cl	IR: No change-No reaction NF$_2$Cl
9001-19B[a]	2.45	1.645 1.709-N$_2$F$_4$	2.569	2.859	Teflon insert in stainless steel	2 hrs., -130°C 16 hrs, R.T.	IR: NOBF$_4$	IR: No change-No reaction NF$_2$Cl, N$_2$F$_4$	IR: No change-No reaction NF$_2$Cl, N$_2$F$_4$
9001-19C[a]	2.50 (NF$_2$Cl + N$_2$F$_4$)	2.859 2.7593		2.445	Teflon insert in stainless steel	67 hrs, R.T.	Elem. Anal.: %F, 60.7, 60.4 IR: NOBF$_4$ X-ray: NOBF$_4$	IR:No change- No reaction NF$_2$Cl,N$_2$F$_4$	IR:No change- No reaction NF$_2$Cl,N$_2$F$_4$

(a) Reactants used recovered from previous experiments.

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Table 78

Reaction of NOBF₄ with NF₂Cl

Experiment No.	Reagents Used NOBF₄	NF₂Cl	Reagents Recovered Solid	Gas	Reactor Type	Experimental Conditions	Product Analysis Solid	Gases	Comments
5001-23A	0.3001	0.3005	0.2798	0.196	Polyethylene insert in stainless steel	72 hrs., R.T.	Elem. Anal.: %F,60.3,62.4 IR:NOBF₄, X-ray: NOBF₄	IR: N₂F₄,N₂O	NF₂Cl completely consumed.
5001-23B	0.4268	0.3450	0.3414	0.178	Teflon insert in stainless steel	72 hrs., R.T.	Elem. Anal.: %F,58.3,59.8 IR:NOBF₄, X-ray: NOBF₄	IR: N₂F₄, N₂O	
5001-23C	0.4387	0.3500	0.1200	0.335	Stainless steel	72 hrs., R.T.	Elem. Anal.: %F,59.6,59.0 IR: NOBF₄, X-ray: NOBF₄	IR: N₂F₄,NF₂Cl Trace NOCl	
5001-28(b)	2.0801	2.146	2.2936	1.556	Teflon insert in stainless steel	18 hrs., R.T. 10 chlorine added	Elem. Anal.: %F,61.5,63.0 %N,13.44,13.12 %B,11.4,10.8 IR:NOBF₄	IR: NOF,N₂F₄, N₂O,NO₂ MS: NOF(47.5%), N₂F₄(16.8%), HCl(18.9%), Cl₂(8.7%),N₂(4.4%), SiF₄(2.1%),N₂O(1.6%)	
5001-30(b)	1.5273	1.338	1.6092	1.787 (includes SO₂)	Teflon insert in stainless steel	2 days, -78°C to -10°C contains 3 ml. of SO₂	IR: NOBF₄	IR: NOCl, N₂F₄, NF₂Cl, SO₂	
5001-32	0.8217	1.215	0.7881		Teflon insert in stainless steel	24 hrs., -46°C to -23°C contains 10 ml. NOCl	IR: NOBF₄	IR: NOCl, NO₂	NF₂Cl completely consummed. No N₂F₄
5001-33(c)	1.11% %F,50.0 %N,9.7 %B,9.2	1.422	1.032	0.626	Teflon insert in stainless steel	20 hrs., R.T. stirred	Elem. Anal.: %F,59,58.9 %N,10.8,10.02 %B,10.6,11.2 IR:Absorptions indicate NO₂BF₄ X-ray: NO₂BF₄ NMR: Nitromethane solution Fluorine signal -BF₄⁻	IR: NOCl, N₂O, NO₂ M.S.: N₂(52.2%), NOCl(25.6%), N₂O(9.5%), HCl(12.5%)	

(b) NOBF₄ from Ozark Mahoning.
(c) Complex mixture obtained from reaction of BF₃ with mixtures of fluorides of nitrogen oxides.

Table 79

Reaction of NOBF$_4$ With ClNF$_2$

Expt. No.	Reactants NOBF$_4$(g.)	NF$_2$Cl(g.)	Reaction Conditions	Analysis * Solid	Effluent Gases	Comments
-57	0.72	0.67	2 hrs. at -130°C. Warmed to room temperature	N, 9.23% F, 84.3%	-	Conducted in glass. Rupture of reactor resulted in loss of gas products.
-61	0.32	~1	Same as -57	N, 15.25;14.85% F, 76.0; 76.1% IR- new absorp. at 4.3 and 13.05 of NOCl	IR-No NF$_2$Cl Increase in concentration of NOCl	Stainless steel reactor with polyethylene insert. Recovered 0.254 gms. solid.
-63	0.38	0.25	24 hours at room temp.	N, 13.68 N, 9.1, 11.3 F, 67.7, 81.1% IR new absorp. at 4.3 and 13.05	Same as -61	Teflon insert used. Recovered 0.37 gms. solid.
-67	0.144	0.165	Same as -57	N, 10.92 F, 74.5, 72.3	IR - NF$_2$ conc. decreased. NOCl conc. increased. M.S. reactant gases. NF$_2$Cl, 12.9 N$_2$F$_4$, 73; HCL, 2.85; NOCl, 0.92; CO$_2$, 10.3 M.S. product gases NF$_2$Cl, 0.0; N$_2$F$_4$, 79; HCl, 0.7; NOCl, 7.3; CO$_2$, 12.9	Teflon Insert - Recovered 0.089 gms. solid
-73	0.23	0.11	Same as -57	N, 9.53 F, 60.9,59.2, 64.4, 60.9 I.R. same as starting NOBF$_4$	I.R. N$_2$F$_4$,NOCl. N$_2$O. M.S. reactant gases NF$_2$Cl, 23.6; N$_2$F$_4$, 65.4; N$_2$O, 5.4; HCL, 3.0; NOCl, 0.0 M.S. product gases NF$_2$Cl, 0.0; N$_2$F$_4$, 24.3; N$_2$O, 11.42; HCl,9.38; NOCl, 54.8	Teflon Insert - Recovered 0.25 gms. solid

↓ Weight of NF$_2$Cl based on mass spectrographic analysis of 13% by weight
↓ Dumas Method:
↓ Devarda alloy Method:
↓ Excess
↓ Theoretical analysis

	% NF$_2$BF$_4$	NOBF$_4$
N	10.7	11.96
F	82.0	64.9

Compound	% F	% N
NOBF$_4$· 2HF	73.3	8.9
NOBF$_4$: 3HF	75.2	7.9
NOBF$_4$· 4HF	77.2	7.1
NOBF$_4$· 5HF	78.8	6.5

However, the calculated nitrogen values are much lower than those found for the products of the reaction which were generally in the range of 9 to 11 per cent. A disquieting result was obtained in Experiment 73, Table 79, where the NOBF$_4$ was recovered unchanged after reaction with NF$_2$Cl. However, mass spectrographic analysis indicated the concentration of NF$_2$Cl in the gas mixture had fallen from 23.6 mole per cent to zero and the concentration of NOCl had gone from zero to 54.8 per cent.

These experiments indicated that in some cases NF$_2$BF$_4$ may have been prepared. However, the lack of correlation between NF$_2$Cl disappearance, NOCl formation, and high fluorine content of solid product was confusing.

A variety of conditions was used in attempts to effect the conversion of nitrosyl fluoroborate to an NF-derivative. The experimental conditions included a study of the effect of variables such as temperature, reaction time, solvents, and the incorporation of contaminants possibly present in the earlier experiments.

It is apparent from an examination of Tables 77 and 78 that nitrosyl fluoroborate is essentially inert to chlorodifluoramine under a wide variety of reaction conditions. Although in many cases complete consumption of the chlorodifluoramine occurred the nitrosyl fluoroborate remained essentially unchanged.

Three different solvents were employed in attempts to increase the reactivity of the nitrosyl fluoroborate. In Experiment 1943-03, Table 77, acetonitrile was used. The chlorodifluoramine was completely consumed and X-ray and infrared examination of the solid remaining on removal of the acetonitrile indicated no change in the starting NOBF$_4$. NMR analysis also showed the presence of only one type of fluorine which was assigned to the BF$_4^-$ group.

In Experiment 5001-30, Table 78, sulfur dioxide was employed and similarly no change in the starting NOBF$_4$ was observed after reaction.

Experiment 5001-32, Table 78, was conducted with NOCl as the liquid phase. The solubility of NOBF$_4$ in NOCl is extremely low so that most of the salt remained undissolved. The chlorodifluoramine was completely consumed but no change in the starting NOBF$_4$ was observed.

Many of the experiments also were conducted at temperatures at which the NF$_2$Cl is in the liquid phase (b.p. -69°C.) so that the NF$_2$Cl was functioning as a solvent. In no case did this appear to cause a change in the starting NOBF$_4$. It appears that in a metal reactor decomposition of

NF_2Cl occurs but there is no reaction with the $NOBF_4$.

To confirm this hypothesis, the reaction of $NOBF_4$ with NF_2Cl was investigated in the Teflon apparatus described in Figure 51 and the results are summarized in Table 81.

In the all Teflon system there was no evidence of a reaction between $NOBF_4$ and NF_2Cl and the NF_2Cl did not decompose to $NOCl$ as observed in metal reactors. It was concluded that the anticipated double decomposition reaction,

$$NF_2Cl + NOBF_4 \longrightarrow NF_2BF + NOCl$$

does not take place under the conditions used.

(f) $NF_2Cl + NO_2BF_4$
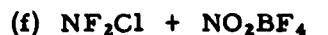
Material

NO_2BF_4. A mixture of NO_2F and BF_3 was bubbled through a solution of BF_3 in Freon -113 at 0°C. A white solid precipitated which was washed with Freon-113 and dried under vacuum. The infrared spectrum of a Nujol mull of the solid was consistent with the spectrum of NO_2BF_4 reported by Sprague, Garrett, and Sisler (70). Analysis showed:

	Found	Theory for NO_2BF_4
Wt. % F	60. 3	57. 2
B	8. 1	8. 1
NO_2^+	35. 5	34. 7

Apparatus

This reaction was investigated in two systems. In the first system, the reactor was constructed of Kel-F and stainless steel as described in Figure 36.

In the second system, the all Teflon reactor described in Figure 51 was used.

Procedure

In a typical experiment using the Kel-F reactor the following procedure was followed.

The salt along with Teflon stirring bar is added to the Kel-F vessel in a dry box and sealed with a stainless steel top. The reactor is attached to a metal vacuum line, evacuated and an excess of NF_2Cl is added at -196°C. The mixture is stirred while being warmed to -130°C. (generally stirred for two hours at -130°C.) or warmed directly to room temperature. The reactants then are stirred for 16 to 24 hours. At the end of this period the effluent gases are condensed, weighed, and analyzed. The reactor

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Table 81

Reaction of $NOBF_4$ with NF_2Cl

Experiment	1891-75
I. Reactant	
$NOBF_4$	0. 86 g.
NF_2Cl	2. 56 g.
II. Experimental Conditions	
Reactor Type	Teflon
Reaction Time	66 hrs.
Agitation	Ultrasonic Vibrator
T°C	
R_1 (a)	30
R_2	-78
III. Products	
$NOBF_4$	0. 83
NF_2Cl	2. 55
IV. Material Balance	98. 1%

(a) Solid reactant was always placed in R_1. R_2 was always open to R_3.

containing the solid is pressured to slightly greater than atmospheric pressure with nitrogen and opened in a dry box.

When the all-Teflon reactor was used, the apparatus was evacuated and filled with H.P. dry nitrogen gas. Solid NO_2BF_4 (0.5 gram) was then placed in the Teflon coil R_1 and the system was evacuated. Approximately 1 gram of NF_2Cl was condensed into Teflon coil R_2 at -196°C. and Teflon coils R_1 and R_2 were isolated from all metal parts by collapsing the tube with a clamp at valve 6. The Teflon coil R_2 was then warmed to -78°C. while R_1 was warmed to 25°C. The solid NO_2BF_4 was held in contact with the gaseous NF_2Cl at 25°C. for 4-50 hours. At 78°C. chlorodifluoroamine exerts a vapor pressure of approximately 400 mm. so that a constant pressure of NF_2Cl was in contact with the solid NO_2BF_4. In some experiments NO_2BF_4 was permitted to stand in liquid NF_2Cl at -78°C. The products were then fractionated and analyzed.

Results

The purpose of this study was to determine whether a double decomposition reaction would occur under the proper conditions to form NF_2BF_4:

$$NO_2BF_4 \ + \ NF_2Cl \longrightarrow NF_2BF_4 \ + \ NO_2Cl$$

The results of experiments conducted in the Kel-F stainless steel reactor are summarized in Table 82. In this reactor chlorodifluoramine reacts with NO_2BF_4 with the formation of a new solid product, as evidenced by a change in the infrared spectrum. The bands at 4.2 and 12.9 microns present in NO_2BF_4, and previously described by Sprague (70), disappear on reaction with NF_2Cl, and a new absorption band at 13.05μ appears. Surprisingly, the gaseous products show the presence of NOCl and no indication of NO_2Cl. Satisfactory material balances could not be achieved because of the significant reaction which apparently was occurring between the metal parts and the reactants. However, only small quantities of inorganic salts contaminated the product as shown in Experiment 11, where the residue, obtained by heating the solid with a Meaker burner, was only 0.36 per cent. Elemental analyses of the solid product were not too informative, although the nitrogen content may have increased slightly as in Experiments 11 and 15. The low fluorine values argued against NF_2BF_4(82%) as a product. Further attempts to establish the structure of the solid were unsuccessful. NMR analysis of a tetramethylenesulfone solution gave identical chemical shifts of B^{11} and F^{19} for both the starting NO_2BF_4 and the product. Only one type of fluorine was detected, eliminating the possibility of NF_2BF_4 being present. Titration with acidic potassium iodide gave a value of 13.6 meg. I_2/gram, which compared to a value of 14.5 meg. I_2/gram for NO_2BF_4.

$$NO_2BF_4 \ + \ KI \longrightarrow I_2$$

Decomposition of the product at 350°C. in a platinum crucible contained in a stainless steel reactor yielded N_2O, NO, NOCl and NO_2 as gaseous products. The absence of fluorine containing materials suggested reaction

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Table 82

Reaction of NO₂BF₄ with NF₂Cl

(Kel-F-steel Reactor)

Expt. No.	Wt. starting NO₂BF₄ (Wt. starting NF₂Cl)	Wt. recovered solid (Wt. recovered gases)	Analysis — Solid				Effluent Gases	
			Elemental	I.R.	X-Ray	Miscellaneous	I.R.	Miscellaneous
2339 -103	0.2634 g. NO₂BF₄ (0.3182)	(0.3911)	% of F, 63.8, 64.5	The characteristic absorptions of NO₂BF₄ at 4.2μ and 12.9μ have disappeared. A new absorption appears at 13.05			N₂F₄, NOCl, CO₂; the NF₂Cl has completely reacted	
5001-3	0.5596 (2.150)	0.5966 (1.6976)	% F, 58.9 Oxid. of KI- 13.6 meq L/g.	See expt. 103	New lines- it is not NO₂BF₄	NMR-spectra of product and starting mat'l showed identical chemical shift for B¹¹ and F¹⁹ as compared to (MeO)₃B and Freon -11	N₂F₄, NOCl, NF₂Cl, (Trace N₂O, CO₂)	Some N₂F₄ and NOCl present in starting NF₂Cl. The N₂F₄ appears to remain approx. the same. The NOCl increases appreciably.
5001-11	1.8586	1.5319	% F, 60.1, 60.5 % B, 10.6 % N, 12.66, 12.4 % Cl, trace Oxid. of KI, 14.5 meq L/g.	See expt. 103	See Expt. 3	Residue on heating in Pt. crucible, 0.36%	NOCl, N₂F₄, N₂O, NO, NF₂Cl	
5001-15	0.2301	0.1400	% F, 60.4 % N, 13.84, 13.55	Peak at 4.2μ present. Peak at 12.9 is missing and new absorption at 13.05μ appears				NOCl, NF₂Cl, N₂F₄

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had occurred with the metal. Decomposition of the product with sodium fluoride produced $NaBF_4$, NO_2 and a small amount of $NOCl$. No evidence for the formation of NO_2F was obtained. The reaction of NO_2BF_4 with sodium fluoride for the synthesis of NO_2F has been reported (72).

$$NO_2BF_4 + NaF \longrightarrow NaBF_4 + NO_2F$$

Only traces of chlorine were found in any of the samples of solid. The properties of the solid are somewhat different from those of the starting NO_2BF_4. The product does not smoke in air; NO_2BF_4 being extremely hydroscopic smokes when exposed. The melting point of NO_2BF_4 is 17°C. with decomposition to its precursors. No noticeable melting of the solid product occurred when heated to 300°C., although considerable decomposition resulted.

Because of the difficulties experienced in obtaining satisfactory material balances, as a result of interferences from the reactor materials, two experiments were conducted in the all-Teflon reactor. The results are summarized in Table 80.

In Experiment 32, the reaction was conducted at 25°C. for four hours. The infrared spectrum of the starting NO_2BF_4 was identical to that of the recovered material. The spectra of the starting and product gases also were identical. The material balance showed a recovery of 98.0 per cent of the NF_2Cl and 100 per cent of the NO_2BF_4. Elemental analysis of the recovered solid also showed no significant changes.

	Recovered Solid	Theoretical NO_2BF_4	Theoretical NF_2BF_4
% F	56.1	57.2	82.1
% N	10.1	10.5	10.1

Since the above reaction had been conducted at room temperature, where the NF_2Cl was present only in the gas phase, the experiment was repeated at -78°C. where the NF_2Cl would be a liquid and could possibly promote reaction by a solvent effect.

$$NO_2BF_4 + NF_2Cl \xrightarrow[\text{50 hrs. Teflon}]{-78°C.} NF_2BF_4 + NO_2Cl$$
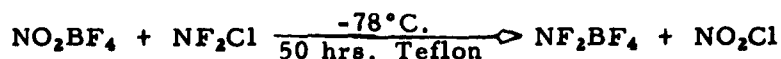
No apparent reaction occurred although the recovery of starting material was not as good as in the earlier experiments. This could be due to handling losses. The recovered NF_2Cl was 88 per cent and the recovered NO_2BF_4 was 80 per cent. An X-ray of the product was consistent only with NO_2BF_4, and no change in the infrared was observed. Elemental analysis again showed no significant change in fluorine content.

	Recovered Solid
% F	55.4
N	10.5
Cl	0.0

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Table 80

Reaction of NO_2BF_4 with NF_2Cl in Teflon

Experiment No.	1891-32	1891-42
I. Reactants		
NO_2BF_4 (g.)	0.476	0.367
NF_2Cl (g.)	0.914	0.856
II. Experiment Conditions		
Reactor Type	Teflon	Teflon
Reaction Time	4 hrs	$50^1/_2$ hrs
Agitation	none	none
T°C R_1 (a)	RT	-78
R_2	- 78	RT
III. Products		
NO_2BF_4 (g.)	0.476	0.295
NF_2Cl (g.)	0.896	0.752
IV. Material Balance	98.7 %	85.6 %

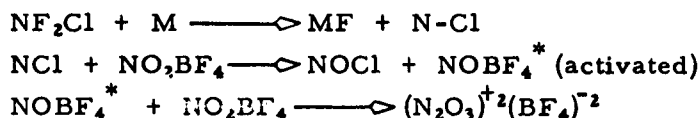| V. Analysis of Solid Product	Found	Theo. NO_2BF_4	Found	Theo. NF_2BF_4
wt.% F	56.1	57.2	55.4	62.1
N	10.2	10.5	10.6	10.5
Cl	-	0	0	0

(a) Solid Reactant was placed in R_1, R_2 was open to R_3

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In the absence of metal no reaction occurs between NO_2BF_4 and NF_2Cl. In a Kel-F reactor attached with metal fittings, NO_2BF_4 reacts with NF_2Cl to produce a new solid. NMR analysis shows the presence of one type of fluorine with a shift identical to the BF_4 group in NO_2BF_4. The oxidizing titer of the product suggests that the number of equivalents of oxidant/gram is close to that for NO_2BF_4. Although X-ray analysis does not detect the presence of NOBFR, the relatively weak absorptions of this material could go undetected at concentrations as high as 20 per cent, so that some NO_2BF_4 may be present. A reasonable reaction scheme in line with all the evidence that has been obtained is presented below. It is proposed that the product may be a new nitrogen oxide cation attached to BF_4^-.

$$NF_2Cl + 2NO_2BF_4 + Metal \longrightarrow MF + NOCl + (N_2O_3)^{+2}(BF_4)^{-2}$$
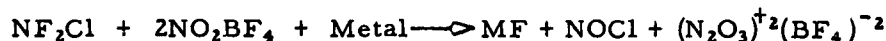
This scheme is in agreement with the NMR, oxidation titer, elemental analysis, and composition of effluent gases.

Since the metal is in contact only with the chlorodifluoramine, and no reaction occurs in the absence of metal, it is necessary to propose intermediate decomposition of the NF_2Cl followed by reaction with NO_2BF_4.

$$NF_2Cl + M \longrightarrow MF + N-Cl$$
$$NCl + NO_2BF_4 \longrightarrow NOCl + NOBF_4^* \text{ (activated)}$$
$$NOBF_4^* + NO_2BF_4 \longrightarrow (N_2O_3)^{+2}(BF_4)^{-2}$$

It was concluded that NO_2BF_4 and NF_2Cl do not react via double decomposition mechanism to yield NF_2BF_4:

$$NO_2BF_4 + NF_2Cl \xrightarrow{\quad/\quad} NF_2BF_4 + NO_2Cl$$

(g) <u>$NF_2Cl + AgNO_3$</u>
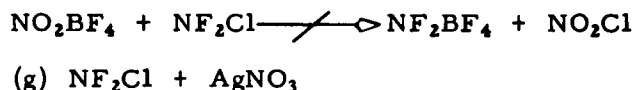
Material

$AgNO_3$. J. T. Baker Chemical Company, Reagent Grade.

C_5H_5N. Allied Chemical and Dye Corp., General Chemical Division.

Apparatus

The reactor consisted of a stainless steel cylinder (200 ml.) which was attached to a general purpose metal high vacuum line.
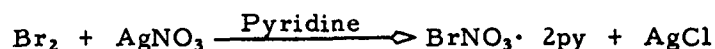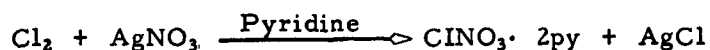
Procedure

In a typical experiment the metal reaction vessel containing a solution of silver nitrate in the cosolvent chloroform-pyridine was attached to the metal vacuum line. The solution was cooled to -78°C. and known weights of tetrafluorohydrazine or chlorodifluoramine were condensed into the vessel. The reaction mixture was warmed to room temperature and maintained for one hour. The vessel then was recooled, the gases recovered and the liquid and gaseous components analyzed.

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Results

Previous work on the synthesis of NF_2NO_3 (Section VI-A, e) indicated that this compound may be relatively unstable, consequently, some means of stabilization was sought.

The stability of a number of halogen compounds can be increased by coordination with pyridine and other organic bases. Thus, chlorine and bromine nitrates can be prepared, complexed with pyridine, by the following reactions:

$$Cl_2 + AgNO_3 \xrightarrow{\text{Pyridine}} ClNO_3 \cdot 2py + AgCl$$

$$Br_2 + AgNO_3 \xrightarrow{\text{Pyridine}} BrNO_3 \cdot 2py + AgCl$$

The nitrates and perchlorates of iodine compounds also have been prepared by similar techniques (78).

$$I_2 + AgNO_3 \xrightarrow{\text{Pyridine}} I(py)_2NO_3$$

$$I_2 + AgClO_4 \xrightarrow{\text{Pyridine}} I(py)_2ClO_4$$
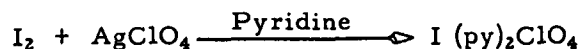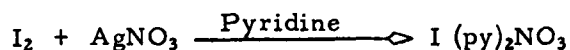
Both the mono- and di-coordinated complexes can be prepared. It is important to note that these complexes offer very significant increases in stability as compared to the parent molecules. For example, the halogen nitrates $ClNO_3$, $BrNO_3$, and INO_3 recently have been prepared and decompose at room temperature. The coordinated halogen nitrates, on the other hand, are solids: $I(py)_2NO_3$ melts at 77.8°C. (79). In electrolysis of the iodine derivatives it has been shown that iodine migrates to the cathode, indicating that the halogens are positive ions, stabilized by coordination.

On the basis of these considerations, work was initiated on the preparation of difluoramine compounds of structures similar to those of the halogen derivatives, stabilized by coordination. The study included the reactions of NF_2Cl and N_2F_4 with $AgNO_3$ in solvents containing basic ligands:

$$NF_2Cl + AgNO_3 \xrightarrow{\text{Pyridine}} NF_2^+ (py) NO_3^- + AgCl$$
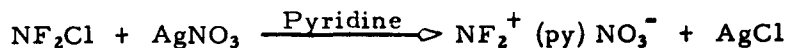
The addition of NF_2Cl to silver nitrate in chloroform-pyridine results in the complete disappearance of NF_2Cl.

$$NF_2Cl + AgNO_3 + \text{pyridine} \xrightarrow{CHCl_3} NF_2(py)NO_3 + AgCl$$
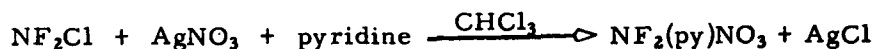
Silver chloride precipitates out and, in Experiment 487, 92 per cent of the silver originally present in $AgNO_3$ was recovered as AgCl. The recovered solution contains very little of the fluorine originally present in NF_2Cl. Only 8.5 per cent of the original fluorine could be recovered in the liquid layer. The liquid did not contain any oxidizer species as evidenced by the absence of oxidation of potassium iodide.

The addition of ether to the reaction solution results in the

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precipitation of a low melting orange solid. Preliminary characterization showed the absence of any fluorine in the solid and only a trace of chlorine. The solid contained significant quantities of nitrate ion along with carbon, hydrogen and additional nitrogen not due to nitrate. The presence of a residue containing silver prevented satisfactory characterization of the impure solid. The results obtained suggest that the solid may contain pyridine nitrate. Apparently some oxidation of the pyridine also occurred, as evidenced by the presence of CO_2 in the gas phase.

The volatile gases condensed from the reaction mixture showed complete disappearance of NF_2Cl. The major products were nitrogen oxides and free nitrogen with some carbon dioxide and N_2F_4.

Since AgCl was isolated, one may conclude that the desired compound formed and then decomposed (reaction path 1, below) or never formed at all (reaction path 2).

1. a. $NF_2Cl + Ag^+(py)NO_3^- \longrightarrow AgCl + NF_2^+(py)NO_3^-$

   b. $NF_2^+(py)NO_3^- \longrightarrow$ Decomposition products

2. a. $NF_2Cl + Ag^+ NO_3^- \longrightarrow AgCl + NF_2\cdot + NO_3\cdot$

   b. $NF_2\cdot + NO_3\cdot + C_5H_5N \longrightarrow$ Decomposition products
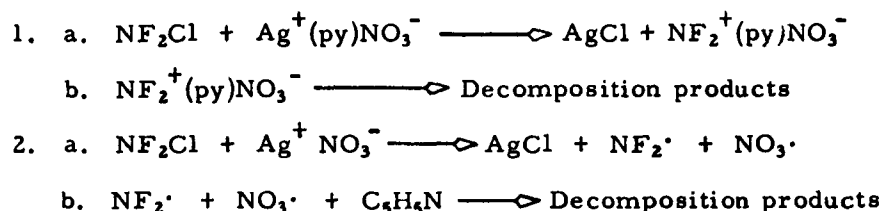
The second path is the familiar redox reaction in which NF_2Cl is prone to participate. Since a satisfactory material balance for fluorine was not achieved (some reaction occurred with the metal reactor) and no N_2F_4 was found in Experiment 487, Table 83, further experimentation was conducted. The use of an oxygen-free anion was considered to prevent any oxidation of the intermediates.

In Experiments 514 and 522, Table 84, silver pyridinium fluoborate, $Ag(py)_2^+BF_4^-$, was employed to minimize oxidation. The salt was prepared by dissolving silver fluoborate in pyridine, followed by removal of the excess pyridine by distillation. In these experiments the reaction temperature was not permitted to rise above 45°C. and the reaction time was held short to minimize any decomposition of the products. The major products again were silver chloride and tetrafluorohydrazine; some chlorodifluoramine was recovered as well.

The usual experimental procedure was to condense the NF_2Cl directly into the chloroform solution containing the silver salt and stir the reaction solution for various times. In Experiment 522, the $Ag(py)_2^+BF_4^-$ dissolved in chloroform was added dropwise to chlorodifluoramine dissolved in chloroform. This procedure would minimize any side reactions between the desired product $NF_2(py)_2^+BF_4^-$ and silver salt. However, the formation of N_2F_4 and AgCl again was observed.

Along with the insoluble silver chloride there also was present a small amount of a second insoluble substance. This was recovered by solution in acetone and, following recrystallization, had a melting point which was in general agreement with that of pyridinium fluoborate salt.

Table 83

Reaction of AgNO₃ with NF₂Cl and N₂F₄

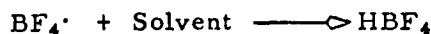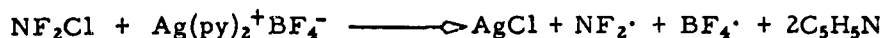| Expt. No.	Reactants	Reaction Conditions	Results
389-480	N_2F_4 (0.73 g.) $AgNO_3$ (1.85 g.) $CHCl_3$ (9 mL.) Pyridine (2 mL.)	1 hour-Room Temp.	N_2F_4 recovered (0.755 g.). IR showed a trace of $CHCl_3$.
389-485	NF_2Cl $AgNO_3$ $CHCl_3$ Pyridine	1 hour- Room Temp.	NF_2Cl completely consumed. M.S. and I.R. Analysis of gas recovered at -78°C. Trace NOCl and possibly N_2O; NO, 59.6%; N_2, 7.9%; $CHCl_3$ 4.1%; CO_2, 33.3%; N_2F_4, 25%. A white solid was separated from reaction liquid and identified as AgCl (x-ray). The reaction liquid does not oxidize KI. IR analysis of liquid showed several unidentified peaks. Addition of ether to liquid produced orange solid. Solid has low m.p. and forms needlelike crystals. Soluble in $CHCl_3$, acetone, sl in H_2O and insoluble in Et_2O, CCl_4. Residue as silver salt 22%. Elemental Analysis: F = 0%; C, 36.70, 36.55 N, 13.60, 13.44 H, 3.94, 3.80 NO_2, 39.6 (8.94%N) Cl - trace
389-487	NF_2Cl (1.06 g.) $AgNO_3$ (1.73 g.) $CHCl_3$ (9 mL.) Pyridine (2 mL.)	NF_2Cl added at -196°C Pressure rose to 18.6 psig at R.T. and then fell to 6.4 psig. Held at R.T. for one hour.	NF_2Cl completely consumed. M.S. and IR. analysis of gas recovered at -78°C. Trace NO_2; NO, 73.2% N_2, 10.6%; $CHCl_3$, 9.9%; CO_2, 6.3%. White solid separated from liquid and identified as AgCl - 92% of the starting silver salt was recovered as AgCl. Liquid does not oxidize KI. Addition of ether to liquid precipitates out orange solid similar to material in Expt. 485. Wt. 0.45 g.
389-495	NF_2Cl (1.37 g.) $AgNO_3$ (1.81 g.) $CHCl_3$ (10 mL.) Pyridine (2 mL.)	Pressure rose to 21.9 psig at R.T. and then fell to 16 psig. Held at R.T. for 2 hours	NF_2Cl completely consumed. IR analysis recovered at -78°C. NOCl, N_2O, NO, N_2F_4, $CHCl_3$; On standing NOCl and N_2F_4 disappeared. Some evidence for NF_2H and NF_3 appeared. Analysis of the liquid for fluorine 1.60, 1.64% which is equiv. to 8.5% of total fluorine present in reactants.

Table 84

Reaction of Silver Pyridinium Salts with NF₂Cl

Experiment No.	Reactants (grams)	m moles	Reaction Conditions	Results
389-490	0.014g AgNO₃ 2.64g pyridine 10 ml CHCl₃ 1.126g NF₂Cl	13.669 33.6 12.87	2 hours at room temp. metal reactor. Transferred -78 to -196	White ppt - AgCl addition of ether to liquid produces orange ppt. probably PyH⁺NO₃⁻ Oxid. titer 0.34 meg.
389-492	1.7874 AgNO₃ 2 ml pyridine 10 ml CHCl₃ 2.847g N₂F₄	10.52 27.37	R.T. - 2 days	Gas was transferred. Contained 1.076g (40.8% orig. N₂F₄) Mostly N₂F₄ - IR liquid reacted with metal IR cell. Orange ppt on addition to ether. Dec. on heating in sublimator
389-498	0.8044 AgNO₃ 1.0538g pyridine 4.7165 CHCl₃ 1.143 NF₂Cl	4.735 13.322 13.07	Kel - F reactor -78°C 16 hours	White ppt - AgCl. Recovered 0.866g gas (75.0%) some non-condensable 0.7... IR gas NOCl, N₂F (major) CH... IR of vapor above material re... NOCl,N₂O,NO,NO₂, CHF...
430514	1.403g Ag(py)₂BF₄ (a) 0.464g NF₂Cl (b) CHCl₃, 14.927g		2 hours at 45°C	Negligible oxidation t... liquid. Gas that was recovered 0.7... contained NF₄Cl (40%), N₂F₄ (60%). Solid contained two components: AgCl, Theor.% Cl. 24.7; found 24.4 Pyridinium fluoborate. m.p 205-213; (Theor. 210-212). Anal.calc.%: C,35.99; H,3.62; N,8.39. Found,%: C,34.89, H,3.71, N,8.38
430522	1.8672g Ag(py)BF₄ 1.114g NF₂Cl 8 ml CHCl₃		2 hours at -45, soln. of Ag(py)₂BF₄ added dropwise with stirring to soln. of NF₂Cl in CHCl₃ at -45°C	Recovered gas (0.6086g). I.R. showed 28% NF₂Cl, 72% N₂F₄. Liquid had negligible oxidation titer. Solid - AgCl and pyridinium fluoborate.

(a) Anal: Theor. Ag(py)₂BF₄: %C, 34.0; %H, 2.85; %N, 7.95; %F, 21.5; Found: %,C, 37.73; %H, 3.20; %N, 7.65; %F, 19.87

(b) IR: 88% NF₂Cl: 12% N₂F₄

The formation of silver chloride, tetrafluorohydrazine, and pyridinium salts from the reaction of chlorodifluoramine with silver pyridinium salts suggests that the reaction course does not proceed via the desired $NF_2(py)_2{}^+BF_4{}^-$, but rather occurs by a redox reaction.

$$NF_2Cl + Ag(py)_2{}^+BF_4{}^- \longrightarrow AgCl + NF_2\cdot + BF_4\cdot + 2C_5H_5N$$

$$BF_4\cdot + Solvent \longrightarrow HBF_4$$

$$HBF_4 + C_5H_5N \longrightarrow C_5H_4NH^+BF_4{}^-$$

$$2NF_2\cdot \longrightarrow N_2F_4$$

Most probably hydrogen abstraction will occur more readily with chloroform than with pyridine and the formation of trichloromethyl radicals is suggested. Although small amounts of other reaction products do form it has not been possible to characterize them further.

Although it is not possible to completely eliminate the possibility that $NF_2(py)_2{}^+BF_4{}^-$ did form and decomposed to produce N_2F_4, this occurrence is less probable.
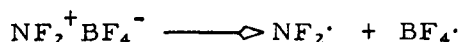
$$NF_2{}^+BF_4{}^- \longrightarrow NF_2\cdot + BF_4\cdot$$

The $BF_4\cdot$ moiety is a more powerful acid than $NF_2\cdot$ and the salt $NF_2{}^+BF_4{}^-$ would not be expected to produce N_2F_4 on decomposition. This would be even less likely in $NF_2(py)_2{}^+BF_4{}^-$. The formation of NF_3 might be expected in this system but this did not occur to any significant extent.

It was concluded that the reaction of NF_2Cl or N_2F_4 with $AgNO_3$ in pyridine or chloroform does not result in the formation of stable difluoramine nitrate adducts. Similarly, the reaction of silver pyridinium fluoborate with chlorodifluoroamine did not result in the formation of stabilized difluoramine pyridinium fluoborate.

No significant reaction occurred over a period of one hour when N_2F_4 was added to silver nitrate dissolved in chloroform-pyridine. The tetrafluorohydrazine was recovered unchanged. There was some evidence that reaction did occur after 48 hours.

h. $NF_2Cl + AgClO_4$
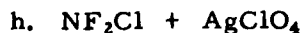
Material

AgClO$_4$. The silver perchlorate was prepared from silver oxide and 70 per cent perchloric acid using the method of Hill (80). Silver perchlorate decomposes on exposure to light and is reported to be shock sensitive. The white crystalline silver perchlorate was dried at 115-120°C. for two hours in a vacuum oven and then stored in amber glass containers in a vacuum dessicator over phosphorus pentoxide.

CH$_3$NO$_2$. Eastman Kodak, Distillation Products Industries, Spectrograde.

Apparatus

The reactor consisted of a Pyrex vessel equipped with a gas dispersion tube and the reactants were stirred with a magnetic stirring bar. The reactor and supporting equipment are described in Figure 49.

Procedure

A solution $AgClO_4$ in nitromethane was placed in the Pyrex reactor and cooled to -196°C. The reactor was evacuated and the solution warmed to room temperature and then pressurized to one atmosphere with chlorodifluoramine. A white precipitate formed immediately and the pressure dropped. The addition of chlorodifluoramine was continued until no pressure drop could be detected fifteen minutes after the addition. The effluent gas was then analyzed by infrared and mass spectrometry. The solid was separated by filtration and examined by infrared, X-ray and for elemental composition. The filtrate was examined by infrared spectroscopy and a portion evaporated to dryness to determine the presence of any dissolved material.

Results

The reaction of chlorodifluoramine with silver perchlorate in nitromethane was investigated in an attempt to prepare NF_2ClO_4.

$$ClNF_2 + AgClO_4 \xrightarrow{CH_3NO_2} AgCl\downarrow + NF_2ClO_4$$
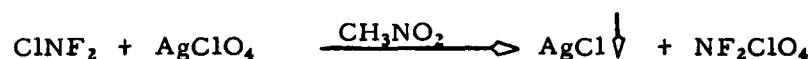
Chlorodifluoramine is known to react with silver chlorate to produce silver chloride (67). This reaction was investigated in water as a solvent and as a solid-gas reaction (Section VI, B, 1, a). Although silver chloride was precipitated immediately in the water system, there was no evidence for the formation of a new N-F compound. The solid-gas reaction produced small amounts of unidentifiable solids in the silver perchlorate matrix which contained nitrogen (2.3%) and fluorine (1.0%). The infrared spectrum of the solid showed a strong absorption in the 11 micron region which was probably due to ClO_3 although an absorption band in this region by an N-F material was possible.

In view of the somewhat encouraging results obtained in the reaction of NF_2Cl with $AgClO_3$, it was decided that the reaction of $AgClO_4$ with NF_2Cl might result in the formation of NF_2ClO_4, particularly if a polar solvent were used. Nitromethane was selected as the solvent. The results of two experiments are summarized in Table 85.

An extremely rapid formation of a solid resulted on the addition of NF_2Cl to a solution of $AgClO_4$ in nitromethane, suggesting that the reaction had proceeded in part by the desired route.

$$NF_2Cl + AgClO_4 \longrightarrow AgCl + [?]$$

This was confirmed by X-ray analysis of the solid (Experiment 2339D-31), which showed the presence of large amounts of silver chloride. Elemental analysis of the solid, however, indicated the absence of any significant

Table 85

Analysis of Products of Reaction of NF_2Cl with $AgClO_4$ in Nitromethane

Expt. No.	Solid	Effluent gases	Solution
2339D-31	X-ray - Only AgCl I.R. - Absorption in 9μ region indicates ClO_4^-. Also absorptions in 10.7 and 11.4 which could indicate N-F. Elemental Analysis: Ag - 42% Cl - 23% N - 1.08% F - .77%	I.R. - N_2F_4	I.R. Only-CH_3NO_2 Present With possibility of trace amounts of an N-O compound
2339D-35	Elemental Analysis: N = 0% F = 0%	I.R. - Only NOCl Mass Spec. - N_2 = 69.2 Mole % NOCl = 18.9 Mole N_2F_4 = 11.8 Mole	I.R. Only solvent and ClO_4^- (AgClO_4 used in excess)

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quantities of a product containing nitrogen and fluorine. In one case nitrogen (1.08%) and fluorine (0.77%) were present; in a second attempt, the insoluble product showed no nitrogen and fluorine, signifying the absence of products such as NF_2ClO_4 in the insoluble phase. Analysis of the solutions showed the absence of materials other than the solvent. The effluent gases showed no unreacted $ClNF_2$; the major products were N_2F_4, NOCl and nitrogen.

It was concluded that in nitromethane a vigorous reaction occurs between NF_2Cl and $AgClO_4$ and silver chloride is precipitated but NF_2ClO_4, the expected product, either did not form or it decomposed readily and could not be isolated from the products. The effect of the glass reactor on this reaction was not determined.

i. $NF_2Cl + Li_3N$

Material

Li$_3$N. K and K Laboratories, Inc., Jamaica, New York.

Diglyme. Olin Mathieson Chemical Corp.

Apparatus

The reactor consisted of a Pyrex glass vessel (about 200 ml. volume) which was attached to a Pyrex glass high vacuum line as described in Figure 49. The reactor was fitted with a gas inlet dispersion tube and the reactants were stirred with a magnetic stirring bar.

Procedure

In a typical experiment, a slurry containing 0.18 g. (5.17 millimoles) of lithium nitride in 100 ml. of Diglyme is placed in the Pyrex reactor and the reactor is attached to the high vacuum line.

The solution is frozen and the reactor is evacuated and 5.22 milli-moles of 98 per cent chlorodifluoramine are added to the reactor. The reactants are stirred for 20 hours at 25°C. The products are then fraction-ated and analyzed.

Results

Koenig et al (81) have reported the use of Diglyme as a medium useful for reactions of lithium nitride. Apparently lithium nitride is sufficiently soluble in Diglyme to permit reactions to take place with the nitride ion. For example, tribenzamide can be prepared from benzoyl chloride and lithium nitride

$$3\emptyset COCl + Li_3N \xrightarrow{\text{Diglyme}} (\emptyset CO)_3N + LiCl$$
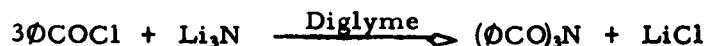
Since the nitride ion is a very strong base, a nucleophillic substitution

reaction on chlorodifluoramine was attempted.

$$Li_3N + 3NF_2Cl \xrightarrow{\text{Diglyme}} (NF_2)_3N + 3LiCl$$

A reaction occurred in this system and the major component in the volatile products was N_2F_4 with about 15 mole per cent being carbon dioxide. The solid which remained on filtration of the solution was shown by X-ray to be mainly lithium nitride with a trace of lithium chloride along with some unknown substance which contributed to strong amorphous scattering of the X-ray pattern. Neither the solution nor the solid oxidized acidic potassium iodide. The recovered Diglyme contained a component volatile at 25°C. which was identified by infrared as methyl formate.

It was concluded that the reaction of chlorodifluoramine with lithium nitride in Diglyme does not produce $(NF_2)_3N$. A complex decomposition occurs to form mainly N_2F_4. A major portion of the Li_3N was recovered although some LiCl was formed.

j. $NF_2Cl + O_3$

Material

O_3. Prepared by decomposition of oxygen in an electric discharge.

Apparatus

The reactor consisted of a 600 ml. all-Teflon vessel which was attached to a general purpose metal high vacuum line.

Procedure

In a typical experiment, the reactor is evacuated, cooled to -78°C. and 0.20 g. of chlorodifluoramine is condensed into the reactor. Ozone, 0.20 g. diluted with helium, is then added to the reactor. The reactor is then closed and the reactants allowed to stand at 25°C. for 16 hours. The products are then fractionated and analyzed.

Results

A direct route to the synthesis of a new oxidizer would be oxidation of chlorodifluoramine with ozone:

$$4NF_2Cl + 4O_3 \longrightarrow NF_2ClO + NF_2ClO_2 + NF_2ClO_3 + NF_2ClO_4$$
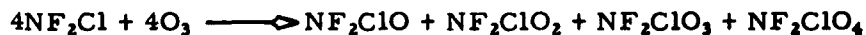
Since ozone has been known to oxidize chlorates to perchlorates (82), this approach was investigated although it was realized that the desired compounds would be relatively unstable.

A reaction occurred but only NOCl, NOF and NO_2 were formed. Complete decomposition of NF_2Cl resulted.

There was no evidence for the presence of any new compound in the products.

C. Reactions with NF₂H

1. Objective

In selecting reactions with difluoramine, its structure and polarizability were considered. It was known that difluoramine shows some basic properties as evidenced by the formation of an adduct with boron trichloride (69) while tetrafluorohydrazine and nitrogen trifluoride do not. It was also known that difluoramine can exhibit acidic properties and is capable of forming weak complexes with ether (84). Although there is no firm evidence that NF_2H undergoes ionization similar to HF, polarization of NF_2H in a direction of lower electron density on the hydrogen atom is expected and consequently, the reactions selected for screening were based on systems designed to produce HF as a by-product and the subsequent coupling of an NF_2 group with some other desirable moiety. A typical reaction that is consistent with these considerations is:

$$NF_2H + FOClO_3 \longrightarrow NF_2OClO_3 + HF$$

Exploratory reactions were conducted with NF_2H and alkali metal chlorates to determine whether an oxidizer could be prepared in this manner. This work was prompted by preliminary laboratory studies which showed that under certain conditions vigorous reactions occurred.

The NF_2H used in this study was prepared by the reaction of N_2F_4 with C_6H_5SH, as described in Section X.

a. NF₂H + KClO₃

Material

KClO₃. American Potash and Chemical Corporation

Apparatus

The reactor consisted of a 100-ml. Vycor vessel attached to a metal high vacuum line.

Procedure

In a typical experiment, 3 grams of $KClO_3$ was placed in the Vycor reactor which was then evacuated and cooled to -78°C. Difluoramine (0.5 gram) was then condensed into the reactor and the reactants were stirred with a magnetic stirring bar for 18 hours at 25°C. The products were then fractionated and analyzed.
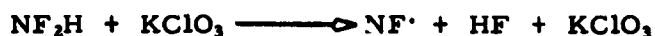
Results

In the presence of metal fluorides, NF_2H decomposes to liberate HF and apparently NF radicals which dimerize to form N_2F_2 (83),

$$2NF_2H + 2KF \longrightarrow N_2F_2 + 2KF \cdot HF$$

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An exploratory experiment was conducted with $KClO_3$ and NF_2H to determine if a somewhat analogous decomposition would occur:

$$NF_2H + KClO_3 \longrightarrow NF\cdot + HF + KClO_3$$

$$NF\cdot + KClO_3 \longrightarrow ClO_3\cdot + KF + 1/2 N_2$$

$$ClO_3\cdot + 2NF_2H \longrightarrow NF_2ClO_3 + 2HF + 1/2N_2$$

$$KClO_3 + 3NF_2H \longrightarrow NF_2ClO_3 + KF + 3HF + N_2$$

The results of this exploratory experiment are summarized in Experiment 1810D-77, Table 86.

A decomposition reaction occurred to form nitrogen oxides and a solid product. Analysis of the solid showed,

		Found	Theoretical for NF_2ClO_3	$KClO_3$
Wt. %	K	34.3	0.0	31.9
	Cl	26.7	26.2	28.9
	N	1.0	10.3	0.0
	F	3.3	28.1	0.0
	O	-	35.4	39.2
			100.0	100.0

While decomposition of the NF_2H occurred, most of the $KClO_3$ was recovered and the low fluorine and nitrogen contents of the recovered solid were attributed to traces of absorbed gases and/or the presence of KF rather than the desired compound.

b. $NF_2H + HClO_4$

Material

$HClO_4$. Anhydrous perchloric acid was prepared by the method of Smith (62). A detailed preparation is given in Section VI, A, 1, g.

Apparatus

The reactor consisted of a Vycor vessel (approximately 100 ml. vol.) attached to a metal high vacuum line.

Procedure

In a typical experiment, 5 grams of anhydrous perchloric acid is distilled into the Vycor reactor and cooled to -78 °C. One gram of NF_2H is then distilled into the reactor; the reactor is cooled, and the reactants are stirred with a magnetic stirring bar for 3 hours at 25°C.

Table 86

General Reactions of Tetrafluorohydrazine and Difluoroamine

Experiment Number	Length of Reaction (hrs.)	Temp. of Reaction °C.	Weight of Reactants (grams)	Analysis of Products	Comments
1810D-75	1.0	25	$\dfrac{HClO_4}{6.5}$ $\dfrac{N_2F_4}{1.2}$	NO_2ClO_4, NO_2, N_2O, ClO_3F, N_2, O_2, Cl_2, HF, NF_3	No reaction at -78°C. however on warming to room temperature a very rapid reaction took place.
1810D-77	18	25	$\dfrac{KClO_3}{3.147}$ $\dfrac{NF_2H}{0.5}$	34.3% K, 26.7% Cl, 1.0% N, 3.3% F.	
1810D-78	3	25	$\dfrac{HClO_4}{5.5}$ $\dfrac{NF_2H}{1.1}$	N_2, O_2, HCl, N_2O, ClO_3F, NF_3 (trace)	No reaction at -78°C - on warming, the reactants decomposed violently.
1810D-80	-	25	$\dfrac{LiClO_3}{3.721}$ $\dfrac{NF_2H}{1.0}$	N_2F_2, O_2, Cl_2, N_2O, NO_2, H_2O.	The reactants exploded on contact.

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Results

This exploratory experiment was conducted to obtain evidence for the formation of NF_2ClO_4,

$$HClO_4 + NF_2H \longrightarrow NF_2ClO_4 + H_2$$
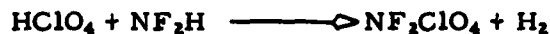
Results are summarized in Table 86, Experiment 1810D-78.

There was no evidence of a reaction at -78°C. but as the reactants were warmed slowly from -78°C. to 25°C. a vigorous reaction occurred to yield only the decomposition products ClO_3F, N_2, HCl, N_2O and NF_3.

c. $NF_2H + ClF_2SbF_6$

Material

ClF_2SbF_6.   Prepared by the solvolysis of SbF_5 in ClF_3.

Apparatus
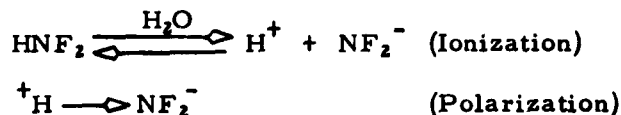
The reactor consisted of a Vycor vessel (about 300 ml. vol.) attached to a general purpose metal high vacuum line.

Procedure

The solid ClF_2SbF_6 (0.0086 mole) was placed in the reactor and the reactor evacuated.   The reactor was then pressured with 0.0276 mole of difluoramine and the reactants were held for several hours at 25°C. The products were then fractionated and analyzed.

Results

It was known that difluoramine has acidic properties and is capable of forming weak complexes with ether (84).   Although the evidence for measurable ionization of NF_2H is questionable (85, 86) polarization of the molecule in a direction of lower electron density on the hydrogen atom appears probable.

$$HNF_2 \underset{\longleftarrow}{\overset{H_2O}{\rightleftharpoons}} H^+ + NF_2^- \quad \text{(Ionization)}$$

$$^+H \longrightarrow NF_2^- \qquad \text{(Polarization)}$$

Reactions with properly constituted reagents, capable of displacing the proton were considered feasible routes to the synthesis of new oxidizers.   The reaction of difluoramine with $ClF_2^+SbF_6^-$ was selected for investigation:

$$HNF_2 + ClF_2SbF_6 \longrightarrow ClF_2NF_2 + SbF_5 + HF$$

When difluoramine was passed over solid ClF_2SbF_6 at 25°C. there was no evidence of a reaction.   The NF_2H was then condensed onto the ClF_2SbF_6 at -125°C.   When the cooling bath was removed, an explosion

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occurred and the product was lost. In a second attempt using 0.0109 mole of HNF_2 and 0.00188 mole of ClF_2SbF_6, a reaction appeared to take place at room temperature as evidenced by a pressure drop. The pressure continued to fall over a period of 2.5 hours, after which it remained constant. A total drop of 307 mm. was observed. The material remaining on the bottom of the reactor was a mixture of solids and a liquid. The following information was obtained.

Effluent gases: I.R. analysis indicated mainly N_2F_4 with a small amount of HNF_2.

Band of white solid on wall: I. R. analysis indicated HF and SbF_6^- bands.

Orange liquid: I. R. analysis showed absorptions for HF and SbF_6^- and two unidentified bands at 7.4 and 12.1 μ.

White solid suspended in liquid: I. R. analysis was similar to that of liquid.

The reaction of difluoramine with $ClF_2^+SbF_6^-$ appeared to proceed mainly by a route leading to the formation of N_2F_4. The formation of HF suggests that catalytic decomposition of the HNF_2 to N_2F_4 is not occurring since hydrogen rather than HF would have formed and a drop in pressure could not have resulted. (However, fluorination of the hydrogen by ClF_2SbF_6 may be a source of the hydrogen fluoride.) The presence of the desired compound ClF_2NF_2 in the crude product was not established.

d. NF_2H + p-Benzoquinone

Material

p-Benzoquinone. Eastman, Distillation Products Industries

Apparatus

The reactor consisted of Pyrex vessel (about 300 ml. vol.) equipped with a magnetic stirring bar.

Procedure

In a typical experiment a solution of recrystallized p-benzoquinone, dissolved in chloroform, is placed in the reactor and the reactor attached to a vacuum manifold. Difluoroamine is then added to the desired pressure and the reactants are stirred for 2 hours at 25°C. The solvent is then cooled to -78°C. and the gaseous products are collected and analyzed. The solvent is analyzed by infrared.

Results

Although the major emphasis on the program was the synthesis of fluorine containing inorganic oxidizers, some exploratory work was conducted with carbon compounds in an attempt to prepare poly NF_2

substituted hydrocarbons. A particularly desirable compound is dodeca (difluoramine) cyclohexane, $C_6(NF_2)_{12}$. A proposed route to this derivative involved the addition of difluoramine to the unsaturated linkage in a quinone. Although several attempts have been made by other investigators to add HNF_2 to the carbonyl of benzoquinone, none had seriously considered 1,4-addition of difluoramine to benzoquinone as the more probable reaction.
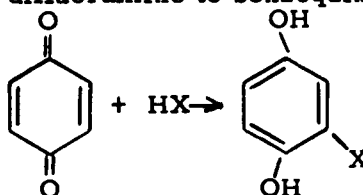
This reaction proceeds readily with a wide variety of reagents including amines, halogen acids, and hydrogen cyanide. The resulting dihydroxy-benzene is readily oxidized so that the product isolated is generally
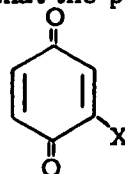
The 1,4-addition may then be repeated until all four hydrogens in benzo-quinone are replaced. The suggested route to $C_6(NF_2)_{12}$ involved this 1,4-addition, employing difluoramine as the HX donor. Since the reaction conditions generally employed for carbonyl addition of HNF_2 are quite different from those used for 1,4-addition, some work with benzoquinone and difluoramine seemed worthwhile.

The results of several experiments are summarized in Table 87.

p-Benzoquinone is inert to difluoramine under conditions during which normal 1,4-addition to the conjugated system occurs with reactants such as the hydrogen acids (87) or amines (88). The p-benzoquinone can be recovered unchanged from the reaction mixture. Addition did not occur when molten benzoquinone (130°C.) was employed in an attempt to force the reaction to proceed at higher temperatures. The presence of a trace of concentrated sulfuric acid produced only tars, and the use of an equivalent of hydrogen chloride did not lead to an induced reaction since no NF materials were present as judged by NMR examination of the products.

An exploratory experiment was conducted with p-benzoquinone and nitroform in an attempt to prepare a polynitro material suitable for further reaction with tetrafluorohydrazine and difluoramine, as shown on the following page.

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Table 87

Reaction of Difluoramine with p-Benzoquinone

| Experiment No.	Conditions					Analysis	
	Catalyst	Solvent	Reaction time (hrs.)	Temp.	Effluent gases	Solution	Solids
2339D-	-	Ether	2	Ambient	N_2F_4; no NF_2H	Peak at 11.3 which disappeared on removal of solvent	I.R. spectra identical to p-benzoquinone
2339D-44	-	-	2.5	115-130°	I.R. N_2F_4, SiF_4; trace N_2O, NO_2, NOCl, NOF	-	I.R. spectra identical to p-benzoquinone
2339D-48-21	One drop conc. H_2SO_4	$CHCl_3$	1	Ambient	-	Only $CHCl_3$ absorptions in I.R. No p-benzoquinone present	p-benzoquinone converted to tars
2339D-48	-	$CHCl_3$	18	Ambient	NOF, NO_2, N_2O	Only $CHCl_3$ and p-benzoquinone absorptions in I.R.	-
2339D-50	Exp. conducted with one equiv. of HCl, 2 equiv. of benzoquinone and 1 equiv. of HNF_2	$CHCl_4$	24	Ambient	I.R.-NO_2, SiF_4; trace N_2O, NOCl	I.R. spectra showed $CHCl_4$ and p-benzoquinone as major components with several unidentified bands. NMR indicates absence of N-F and presence of some C-F material.	-
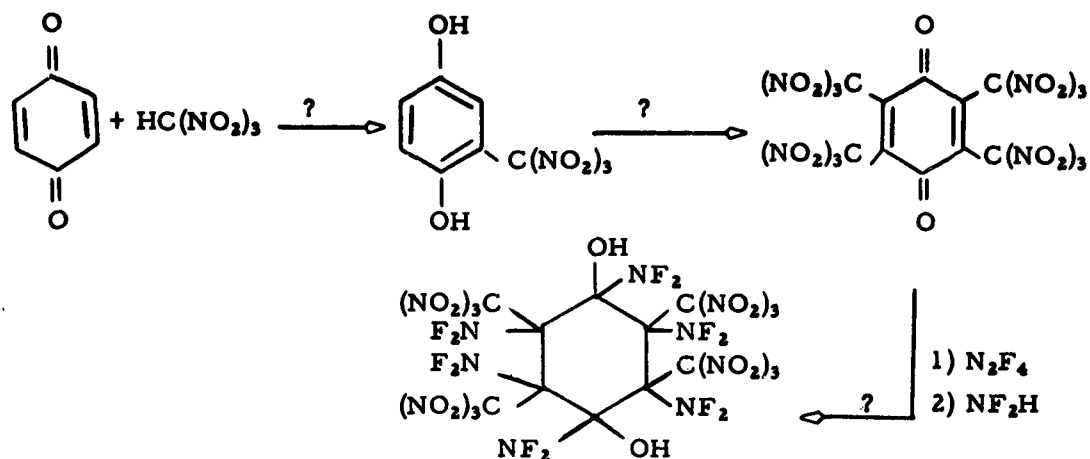
The reaction conditions were:

1) stirring for 24 hours at 25°C.

2) refluxing for 7 1/2 hours

3) adding a trace of sulfuric acid and then refluxing

In the absence of sulfuric acid there was no reaction. The infrared spectra of the solutions corresponded to standards prepared for the reactants. The addition of sulfuric acid resulted in some tar formation, but the materials remaining in solution consisted only of chloroform and nitroform.

D. **Reactions with NF₃**

1. **Objective**

Of the known N-F compounds, nitrogen trifluoride is the most thermally stable and least reactive. However, in spite of its inherent stability, when it is sufficiently activated it has the advantage of providing a fluorine atom for the formation of stable fluorides with the concomitant liberation of an NF_2 radical. This is illustrated in the reaction of NF_3 with copper at 500°C.

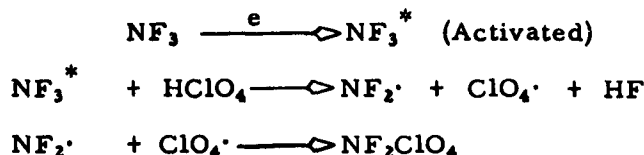$$2NF_3 + Cu \xrightarrow{500°C.} 2NF_2\cdot + CuF_2$$
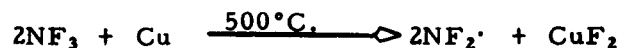
Most of the known reactions with NF_3 however require high temperatures, a distinct disadvantage for the synthesis of high energy oxidizers since such oxidizers are not likely to be stable at high temperatures.

We reasoned that NF_3 might be used for the synthesis of high energy oxidizers by activating only the NF_3 and then permitting the activated NF_3 to react with less stable species such as anhydrous perchloric

acid, followed by rapid quenching of the products at -196°C. For example,

$$NF_3 \xrightarrow{\quad e \quad} NF_3^* \text{ (Activated)}$$

$$NF_3^* + HClO_4 \longrightarrow NF_2 \cdot + ClO_4 \cdot + HF$$

$$NF_2 \cdot + ClO_4 \cdot \longrightarrow NF_2ClO_4$$

Most of the reactions selected for investigation involved vigorous activation of the NF_3, either thermally or by electric discharge. Several exploratory reactions designed to produce novel intermediates such as $NaNF_2$, NF_2BF_4 and NF_2PF_6 were also investigated.

a. $NF_3 + HClO_4$

Material

NF_3. Peninsular Chemical Research Corporation

$HClO_4$. Anhydrous perchloric acid was prepared by the method of Smith (62). A detailed preparation is given in Section VI, A, 1, g.

Apparatus

This reaction was conducted in an electric discharge apparatus which was modified for specific experiments. The three basic designs used are shown in Figure 35.

Procedure

In a typical experiment NF_3 is metered into the discharge tube through a capillary flowmeter. The activated NF_3 gas stream is then merged with a gas stream of anhydrous perchloric acid (not activated by the electric discharge) and the reaction products are quenched rapidly in Pyrex glass traps cooled to -196°C. The products are then fractionated and analyzed.

Results

In most of these experiments, NF_3 was passed through the discharge tube and the activated NF_3 reacted with anhydrous perchloric acid. Rapid quenching of the products was considered to be critical if the compound NF_2ClO_4 is thermally unstable.

The results of a series of experiments are listed in Tables 88 and 60.

Although the reaction of activated NF_3 with anhydrous $HClO_4$ did not produce a solid product containing fluorine the volatile products in some experiments showed the presence of absorption bands in the 10-12 micron region which were believed to be due to N-F bonding. However, the formation of these unidentified volatile products was not consistent and generally the effluent gases were composed of nitrogen oxides, SiF_4

Table 88

Electric Discharge Tube Reactions

Experiment Number	Time	Voltage	Flow Rate of NF$_3$ ml/min.	Flow Rate of HClO$_4$ ml/min.	System Pressure mm.	Temp. of Tube °C	Weight of Product	Analysis of Solid	Volatile Products
1810D-32	1/3 hr.	15,000	40	35	1.5	(A)	< 0.1 g.	(B)	NO, NO$_2$, N$_2$O, SiF$_4$, Chlorine oxides N$_2$F$_2$
1810D-34	1 hr.	15,000	50	25	1.7	0	~ 0.2 g.	1.33%Cl 1.35%F (C)(+D)	NO, NO$_2$, N$_2$O, SiF$_4$, Chlorine oxides N$_2$F$_2$
1810D-35	1 hr.	15,000	50	25	1.7	0	~0.25g.	5.98%N	N$_2$O, NO, NO$_2$, SiF$_4$, Chlorine oxides N$_2$F$_2$
1810D-36 (E)	3/4 hr.	15,000	40	30	1.2	(F)	0.3 g.	0.60% F 8.73%Cl	Not analyzed

(A) Reaction tube initially at room temperature. During discharging, temperature exceeded 100°C.

(B) Insufficient solid for quantitative analysis. Positive KI Test.

(C) No analysis for ClO$_4^-$.

(D) NO$_2$ evolved on hydrolysis.

(E) Modified discharge tube used

(F) Tube cooled to -78°C.

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N_2F_2 and chlorine oxides. Small amounts of solid product were identified as NO_2ClO_4.

The presence of considerable quantities of SiF_4 in the product coupled with the observed etched surface of the discharge tube was discouraging. It appeared either that the conditions were too energetic and complete dissociation of the NF_3 occurred in the 15000 volt discharge field or that the products were extremely unstable and could not be isolated under these conditions.

b. NF_3 + Na

Material

NF_3. Prepared by the elctrolysis of NH_4F in HF.

Na. Fisher Scientific Co.

Apparatus

The high pressure apparatus is described in Figure 52. The reactor consisted of a 100-ml. stainless steel Magne Dash autoclave.

Procedure

In the study of the high pressure reaction of nitrogen trifluoride with metallic sodium, 6.619 g. (0.121 mole) of purified nitrogen trifluoride (prepared in the Olin Mathieson laboratories) was distilled into a 100-ml. Magne Dash autoclave at -196°C. After the cooling bath was removed, the autoclave pressure was 11.2 atmospheres. The system was then pressurized to 80 atmospheres with nitrogen. The resulting mole ratio of materials in the system was N_2: Na:NF_3=2:4:1.

The reactor was heated from room temperature to 250°C. over a period of 8 hours. During the heating period the measured pressures were checked against those calculated and approximate agreement was taken to indicate no reaction. At 200°C. a sharp deviation in the pressure curves occurred, and at 250°C. the experiment was terminated, (see Figure 53). At the conclusion of the experiment the reaction gases were passed through traps cooled to -78°C. (Dry Ice), -130°C. (n-pentane slush), and -196°C. (liquid nitrogen) and analyzed. The solid product was also collected and analyzed.

### Results

The objective of this work was to prepare the compound $NaNF_2$,

$$Na + NF_3 \xrightarrow{\quad 250°C. \quad} NaNF_2 + NaF$$
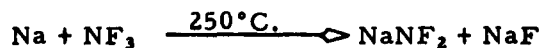
During the heating cycle from 25°C. to 250°C. the pressure of the reactor was checked against the calculated pressure for the system assuming no reaction. The calculated pressures were compared to the observed pressure and any deviation from calculated pressure was attributed to a

Figure 52

Apparatus for High Pressure Reactions with Nitrogen Trifluoride
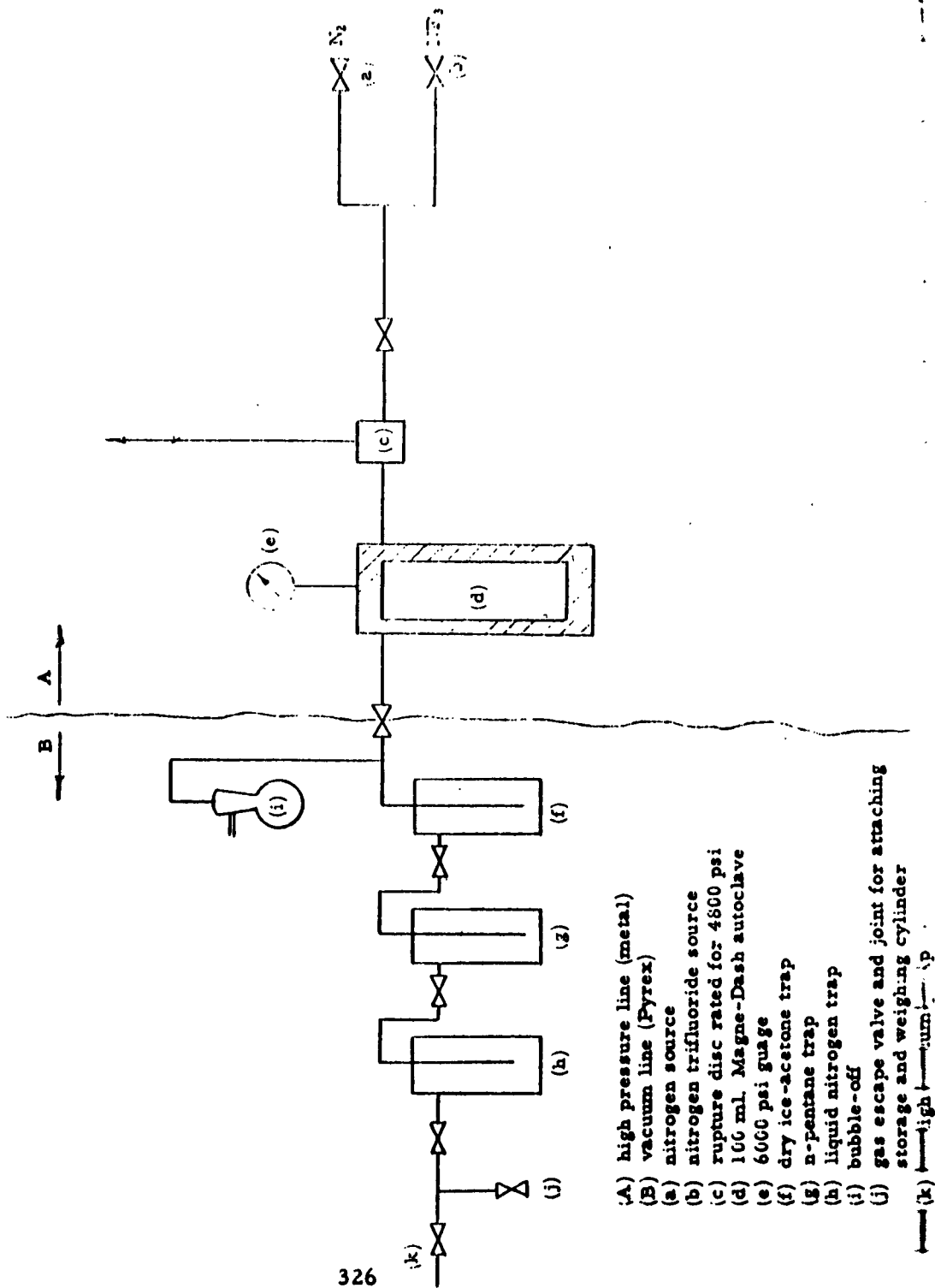
(A) high pressure line (metal)
(B) vacuum line (Pyrex)
(a) nitrogen source
(b) nitrogen trifluoride source
(c) rupture disc rated for 4800 psi
(d) 100 ml. Magne-Dash autoclave
(e) 6000 psi gauge
(f) dry ice-acetone trap
(g) n-pentane trap
(h) liquid nitrogen trap
(i) bubble-off
(j) gas escape valve and joint for attaching storage and weighing cylinder
(k) ⊢high ⊢vacuum⊣ ⊢p

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Figure 53

High Pressure Reaction Between Nitrogen Trifluoride and Metallic Sodium

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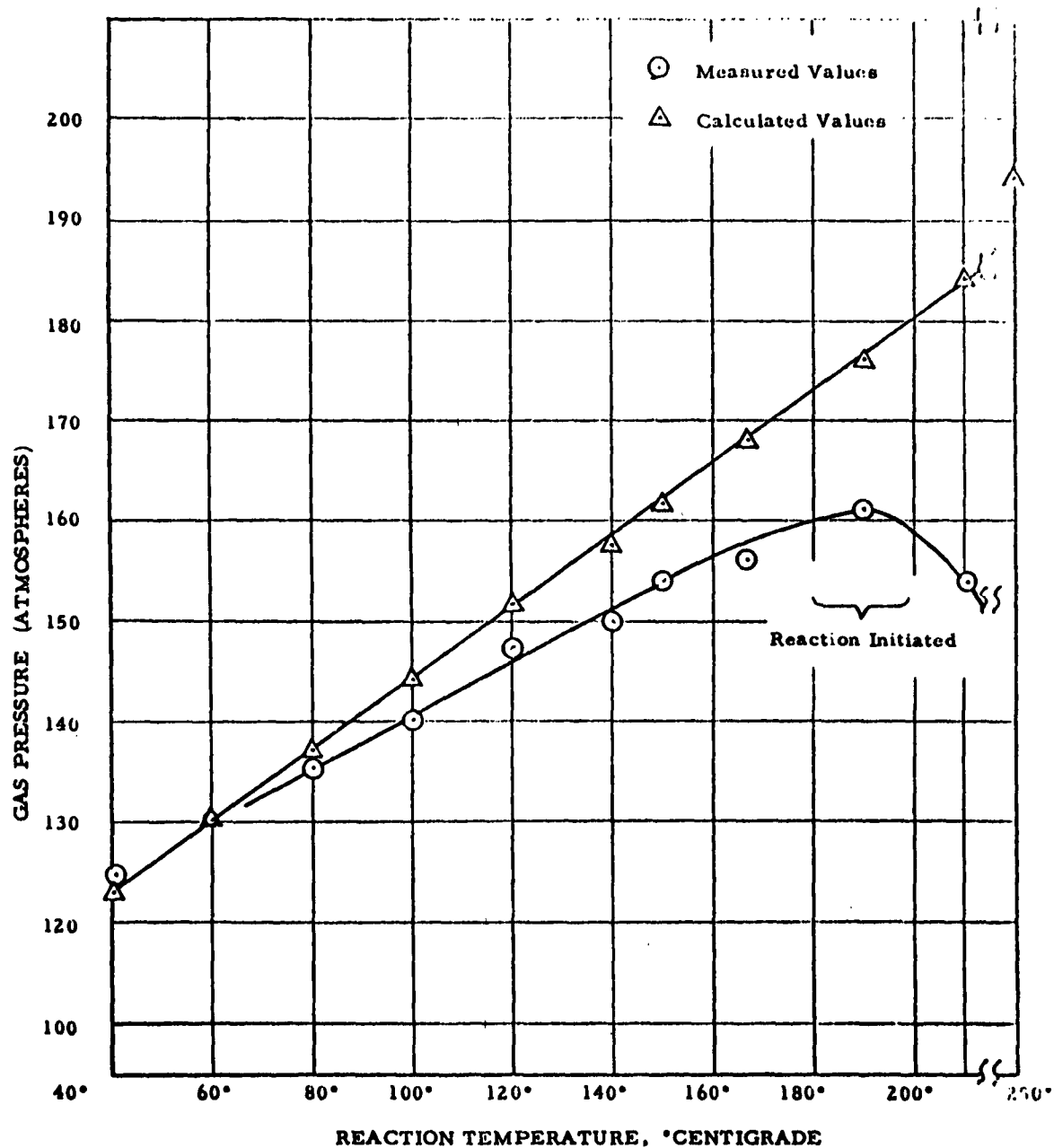
CONFIDENTIAL

reaction. The pressure vs. temperature plot is shown in Figure 53.

A reaction occurred at approximately 190°C. between nitrogen tri-fluoride and metallic sodium. Only 3.085 grams of NF_3 was recovered out of a total 6.619 grams which corresponds to a 53.4 per cent conversion of NF_3. A white crystalline product (1.321 g.) was recovered from the upper walls and top of the autoclave. This material had apparently sublimed onto these cooler regions of the autoclave during reaction.

Analysis of the solid showed the following,

		Found	$NaNF_2$	Theory ($NaNF_2$ + NaF)	(4NaF + Na_3N)
Wt. %	F	$30.4^+-1.0$	50.67	48.72	30.29
	N	$5.8^+-0.3$	18.67	11.97	5.58
	Na	-	30.66	39.31	64.13
			100.00	100.00	100.00

The solid product appears to be a mixture of 4NaF + Na_3N. This solid dissolved in water without gas evolution and the solution did not liberate iodine with neutral potassium iodide solution.

It was concluded that the reaction of NF_3 with metallic sodium results in the formation of NaF and Na_3N rather than $NaNF_2$. It was not established whether $NaNF_2$ is an unstable intermediate which decomposes to NaF.

c. $NF_3 + BF_3$

Material

NF₃. Air Products, Inc.

BF₃. The Matheson Co., Inc.

Apparatus

The apparatus consisted of a nickel reactor, Figure 2, which was attached to a general purpose metal high vacuum line.

Procedure

The reactor was evacuated and cooled to -196°C. Nitrogen tri-fluoride, 13.0737 g. (0.184 mole) and 10.3117 g. (0.152 mole) of BF_3 were distilled into the reactor. The molar ratio of BF_3-NF_3 was 1/1.2.

The reactants were placed on a mechanical agitator and shaken for 48 hours at 160°C. At 160°C. the pressure increased to 900 psi. The reactor was then cooled to 25°C. and the products were fractionated and analyzed.

Results

The objective of this experiment was to determine whether NF_3 would form a simple adduct with BF_3, or possibly, the compound NF_2BF_4.

$$NF_3 + BF_3 \longrightarrow NF_2BF_4$$

The results are summarized in Experiment 1089D-3, Table 8.

There was no evidence of a reaction under the conditions employed. Essentially all of the BF_3 and NF_3 were recovered and identified. The material accountability was 99 per cent. It was concluded that under these conditions, NF_3 has no basic properties since there was no evidence of an adduct formation.

d. $\underline{NF_3 + PF_5}$

Material

NF_3. Air Products, Inc.

PF_5. Prepared by the following reaction,
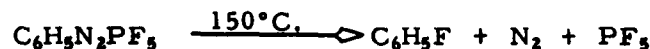
$$C_6H_5N_2PF_5 \xrightarrow{\text{150°C,}} C_6H_5F + N_2 + PF_5$$

Apparatus

The apparatus consisted of a nickel reactor, Figure 2, which was attached to a general purpose metal high vacuum line.

Procedure

The reactor was evacuated and cooled to -190°C. Phosphorous pentafluoride, 10.5916 g. (0.08415 mole) followed by 9.6551 g. (0.136 mole) of NF_3 was distilled into the reactor and the reactor closed. It was then placed on a mechanical agitator and shaken for 48 hours at 200°C. The products were then fractionated and analyzed.

Results

While NF_3 was known to be a very stable compound it was thought that at high temperature and pressures the following reaction might occur,

$$NF_3 + PF_5 \xrightarrow{\text{200°C.}} NF_2{}^+PF_6{}^-$$
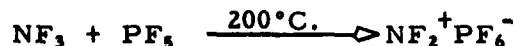
Even though NF_2PF_6 would not be a candidate high energy oxidizer it was hoped that a study of this reaction would provide data on the conditions required to induce reactions with NF_3 for other exploratory studies.

The results of this work are summarized in Experiment 1876D-94, Table 8.

There was no evidence of a reaction. All of the NF_3 and PF_5 were recovered and identified. The material accountability was essentially 100 per cent.

e. NF₃ + Cl₂

Material

NF₃. Peninsular Chemical Research Corporation

Cl₂. The Matheson Co., Inc. Purity 99.8%.

Apparatus

This reaction was investigated in the electric discharge apparatus described in Figure 35.

Procedure

In a typical experiment a mixture of NF_3 and Cl_2 is metered into the discharge tube and the products are quenched rapidly in a series of Pyrex traps cooled to -196°C. The products are then fractionated and analyzed.

Results

This exploratory experiment was conducted to determine whether electric discharge activation of NF_3 and Cl_2 would result in the formation of NF_2Cl.

$$NF_3 + Cl_2 \xrightarrow{\quad e \quad} NF_2Cl + FCl$$

The results are summarized in Experiment 1810D-53, Table 60.

Volatile products consisted mainly of Cl_2, NF_3, NO_2 and SiF_4. There was no evidence for the presence of NF_2Cl or FCl in the products. The infrared analysis of the volatile products showed several absorption bands which were not identified.

f. NF₃ + N₂F₄, O₂

Material

NF₃. Air Products, Inc.

N₂F₄. E. I. DuPont de Nemours and Co., Inc. Purity 99%⁺.

Apparatus

The electric discharge apparatus is described in Figure 42.

The gases were subjected to an electrical discharge at 5-15 KV in an evacuated system. The reactor was a U-tube made of quartz or Pyrex

and the electrodes were Monel metal rods 2 mm. in diameter. The electrode gap varied in the experiments between 3 and 12 cm. The vacuum line was a metallic type (copper tubing, brass sleeves and joints, nickel valves, Monel traps) except for the 500 ml. storage bulb made of Pyrex glass. The line was flamed and evacuated before each experiment. The newly assembled line was fluorinated for 24 hours with chlorine trifluoride before use.

Lubricants were avoided wherever possible and Kel-F fluorocarbon grease was employed when necessary. The Pyrex storage bulb served as a reservoir of reactant gases and could be filled and evacuated through a 3-way vacuum stopcock. The pressure was estimated with two metal vacuum gauges, which were checked with a McLeod gauge and found to be reliable down to 0.25" vacuum.

Procedure

The storage bulb is filled with the reactant mixture to a total pressure of one atmosphere; the remaining portion of the line is under vacuum. A coolant is placed around the reactor and a bath of liquid nitrogen around trap 1. The discharge is started producing a continuous, broad, bluish-pink band between the electrodes. Valve 1 is closed and the stopcock for the storage bulb is opened. Needle valve 1 is now slowly opened which permits the gas mixture to flow into the reactor, during which time valve 6 is closed. The discharge assumes a deep purple color. Needle valve 1 maintains the gas flow at a pressure drop of about 1/2" to 1" per minute, as measured on gauge 1. Needle valve 6 is then opened so that the pressure reading on gauge 2 is about 1/2" to 1 3/4", a pressure sufficient to maintain an even flow and valves 1, 2, 3, 4 and 6 are closed and the discharge is turned off. A brown solid is generally visible in the reactor. The products are then permitted to warm and are recondensed at -196°C. This decomposes any of the higher fluorine oxides. Bulb to bulb fractional distillation then is conducted and the various gas fractions are analyzed by infrared spectrometry.

Results

A number of exploratory reactions was conducted with electric discharge activated NF_3 to promote the formation of new N-F compounds. Possible reactions with N_2F_4 are,

$$NF_3 + N_2F_4 \xrightarrow{\quad e \quad} NF_4^+ NFNF_2^-$$

or

$$3NF_3 + N_2F_4 \longrightarrow N(NF_2)_3 + 7/2F_2 + 1/2 N_2$$
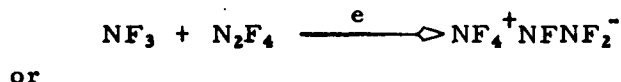
The results of two experiments, 19 and 20, are summarized in Table 52.

The volatile products consisted of NF_3, N_2F_4 and traces of NOF and N_2O. There was no evidence of interaction between NF_3 and N_2F_4. Most of the reactants were recovered.

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When NF$_3$ and oxygen were passed through the discharge tube the
volatile products consisted of NF$_3$ and N$_2$O. The results of this reaction
are summarized in Experiment 18, Table 52.

Section VII.   Reactions With MNClO$_3$ Compounds

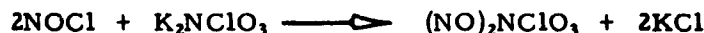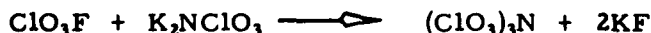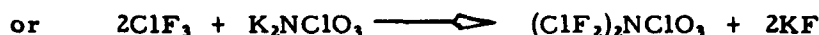A.   Reactions With K$_2$NClO$_3$

1.   Objective

Potassium nitridochlorate (VII), K$_2$NClO$_3$, is a white crystalline solid that is extremely shock sensitive when pure and dry. Some earlier attempts to fluorinate this compound with fluorine gas resulted in explosion.

The fluorination of this compound was particularly attractive since the reaction of fluorine with solid metal chlorates is well known (52) and it was anticipated that this compound might fluorinate in a similar manner:

$$F_2(g) \ + \ KClO_3(s) \longrightarrow KF \ + \ FClO_3$$

$$F_2(g) \ + \ K_2NClO_{3(s)} \longrightarrow NF_2ClO_3 \ + \ 2KF$$
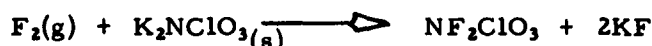
In view of the extreme reactivity of K$_2$NClO$_3$ with fluorine, fluorination of this compound with NF$_3$ and ClF$_3$ was investigated. The objective here was to prepare solid fluorine containing oxidizers:

$$2NF_3 \ + \ K_2NClO_3 \longrightarrow (NF_2)_2NClO_3 \ + \ 2KF$$

$$2ClF_3 \ + \ K_2NClO_3 \longrightarrow NF_2ClO_3 \ + \ 2KF \ + \ 2ClF$$

$$\text{or} \qquad 2ClF_3 \ + \ K_2NClO_3 \longrightarrow (ClF_2)_2NClO_3 \ + \ 2KF$$

$$ClO_3F \ + \ K_2NClO_3 \longrightarrow (ClO_3)_3N \ + \ 2KF$$

$$2NOCl \ + \ K_2NClO_3 \longrightarrow (NO)_2NClO_3 \ + \ 2KCl$$

These reactions were selected for study since very little was known about the reactivity of K$_2$NClO$_3$ and the reactions appeared to be reasonable on the basis of analogous fluorination of metal chlorates. The formation of KF was expected to provide the driving force for the formation of the less stable compounds.

In a second approach to new derivatives, if a satisfactory solvent could be found, simple metathetical reactions with other salts were considered i.e.:

$$K_2NClO_3 \ + \ 2ClF_2SbF_6 \xrightarrow{\text{Solvent}} 2KSbF_6 \ + \ (ClF_2)_2NClO_3$$

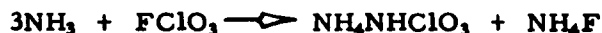$$K_2NClO_3 \ + \ 2NO_2BF_4 \xrightarrow{\text{Solvent}} (NO_2)_2NClO_3 \ + \ 2KBF_4$$

A variety of solvents was screened although the reactivity of these reagents imposed vigorous limitations on the number of possible solvents.

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a. $K_2NClO_3 + NF_3$

Material

NF_3, Air Products, Inc., purity 98%[+]

K_2NClO_3. Prepared by the following reactions:

$$3NH_3 + FClO_3 \longrightarrow NH_4NHClO_3 + NH_4F$$

$$NH_4NHClO_3 + KOH \xrightarrow[H_2O]{NH_4OH} K_2NClO_3 + NH_3 + H_2O$$

The solid K_2NClO_3 was washed with methanol and dried in a vacuum oven at 25°C. for 18 hours. Elemental analysis of the product showed:

|		Found	Theory for K_2NClO_3
Wt. %	K	48.8	44.5
	N	8.3	8.0
	Cl	18.9	20.2
	O	—	27.3
			100.0

Apparatus

The reactor consisted of a Teflon vessel with an exposed stainless steel top as described in Figure 54. This reactor was attached to a general purpose high vacuum line.

Procedure

In a typical experiment, 0.2 gram of the dried salt, K_2NClO_3, was placed in the Teflon reactor, and the reactor was attached to the high vacuum line and evacuated. The reactor was then cooled to -196°C. and approximately 4 grams of NF_3 was distilled into the reactor. The reactor was then warmed to 25°C. and allowed to stand for 18 hours. The products were then fractionated and analyzed.

Results

The purpose of this exploratory experiment was to determine whether K_2NClO_3 and NF_3 would react as follows:

$$K_2NClO_3 + NF_3 \xrightarrow{25°C.} (NF_2)_2NClO_3 + 2KF$$
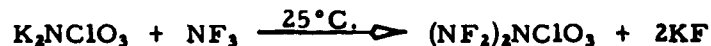
There was no evidence of a reaction. All of the NF_3 and K_2NClO_3 were recovered unchanged.
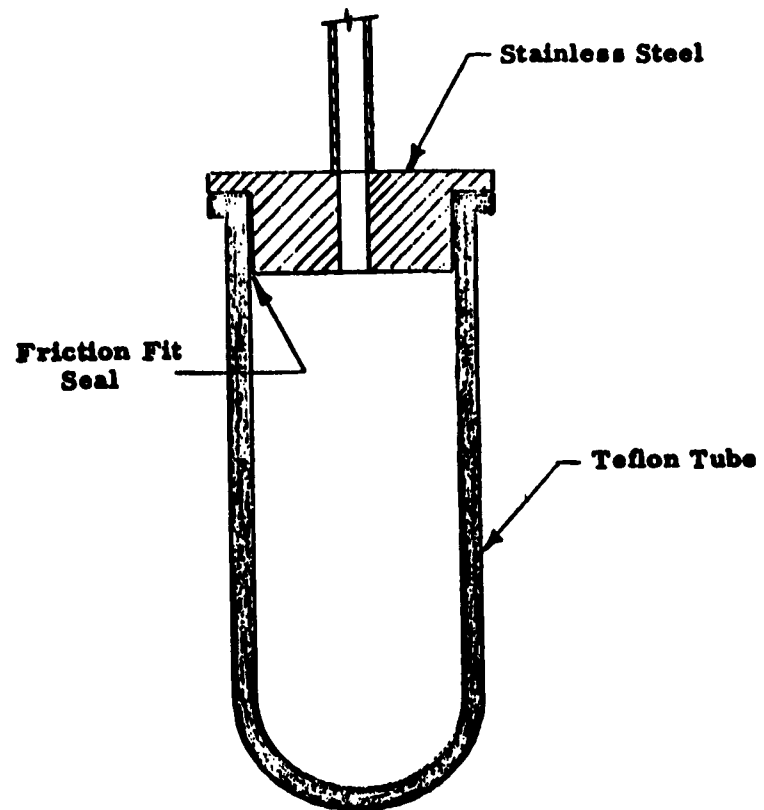
b. $K_2NClO_3 + FClO_3$

Material

$FClO_3$, Pennsalt Chemical Co., purity 99%

K_2NClO_3. Prepared as described previously.

Figure 54

Teflon Reactor

Stainless Steel

Friction Fit
Seal

Teflon Tube

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Apparatus

The reactor consisted of the Teflon vessel, Figure 54, attached to a general purpose metal high vacuum line.

Procedure

In a typical experiment 0.2 gram of K_2NClO_3 was placed in the reactor and the reactor attached to the high vacuum line. The reactor was then evacuated, cooled to -78°C. and approximately 3 grams of $FClO_3$ was distilled into the reactor. The reactor was then closed and the reactants were permitted to stand for 18 hours at 25°C. The products and/or reactants were then fractionated and analyzed.

Results

The desired reaction was:

$$2FClO_3 + K_2NClO_3 \xrightarrow{25°C.} (ClO_3)_3N + 2KF$$
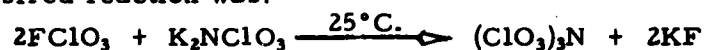
There was no evidence of any reaction under these conditions. All of the reactants were recovered unchanged and identified by infrared, and element analyses.

c. $K_2NClO_3 + ClF_3$

Material

ClF_3, The Matheson Co., Inc.

K_2NClO_3. Prepared as described.

Apparatus

The reactor, Figure 54, was the same as that used for the previous reactions with K_2NClO_3.

Procedure

In a typical experiment, 0.2 gram of dried K_2NClO_3 was placed in the reactor and the reactor attached to the high vacuum line and evacuated. The reactor was then cooled to -78°C. and approximately 4 grams of ClF_3 was distilled into the reactor. The reactor was then warmed to 25°C.

Results

The fluorination of K_2NClO_3 with ClF_3 presented interesting possibilities since the reaction could result in the formation of NF_2ClO_3 or $(ClF_2)_2NClO_3$.

$$2ClF_3 + K_2NClO_3 \longrightarrow (ClF_2)_2NClO_3 + 2KF$$

$$ClF_3 + K_2NClO_3 \longrightarrow NF_2ClO_3 + 2KF + 2ClF$$
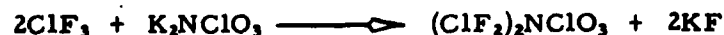
A vigorous reaction occurred at -78°C., or slightly above, and repeated efforts to control this reaction resulted in violent explosions. In all

instances the products appeared to be completely decomposed and not recoverable.

d. K_2NClO_3 + NOCl

Material

NOCl, The Matheson Co., Inc.

K_2NClO_3. Prepared as described.

Apparatus

The reactor was constructed of Pyrex glass, Monel, and nickel, as described in Figure 55. This reactor was attached to a general purpose metal high vacuum line.

Procedure

In a typical experiment 0.7 gram of dried K_2NClO_3 was placed in the Pyrex reactor, the reactor attached to the high vacuum line and all volatile products pumped off. The reactor was then cooled to -78°C. and 8 grams of NOCl distilled into the reactor. The reactor was then closed and the reactants were held at 25°C. for 72 hours. The products and/or reactants were then fractionated and analyzed.

Results

The primary purpose of this work was to prepare the compound $(NO)_2NClO_3$ by the following reaction:

$$2NOCl + K_2NClO_3 \longrightarrow (NO)_2NClO_3 + 2KCl$$

A slow reaction occurred at 25°C. to form a solid product. Infrared analysis of the effluent gases showed only NOCl and traces of nitrogen oxides.

The recovered solid showed a net gain in weight, i.e.

0.9939 g.	Solid Recovered
0.7658 g.	K_2NClO_3 Added
0.2281 g.	Gain

Theoretical gain in weight of solid, based on the proposed reaction, would be 0.427 g. If it is assumed that the reaction occurred as proposed above, the conversion of K_2NClO_3 would be 53.4%. Elemental analysis of the crude solid showed:

Wt. %		Found	Theory For $(NO)_2NClO_3$	K_2NClO_3	F_2NClO_3 + 1.068 NOCl
	K	38.1	-	44.5	31.8
	N	8.5	26.7	8.0	11.8
	Cl	12.9	22.5	20.2	29.9
	O	-	50.8	27.3	26.5
			100.0	100.0	100.0

* Based on 53.4% conversion of K_2NClO_3 to $(NO)_2NClO_3$

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Figure 55

Pyrex Reactor

Vac Line

Monel & Nickel
construction

Teflon
gasket

1" Pyrex pipe oap

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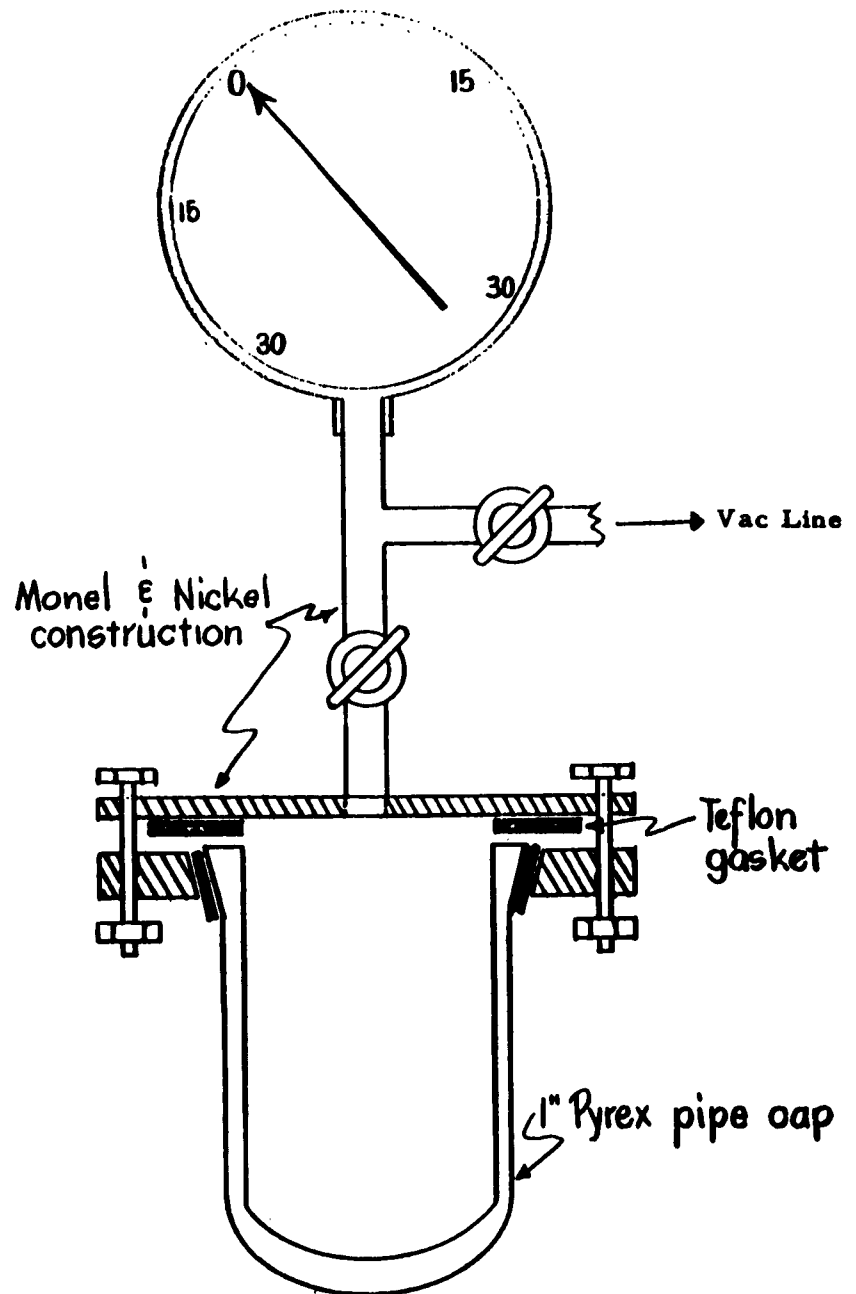
The results of this study were inconclusive. Additional investigation on the final product is needed to establish whether the reaction occurred as proposed. The reactivity of the recovered solid and the shock sensitivity of K_2NClO_3 precluded the preparation of mulls for infrared examination.

e. K_2NClO_3 + $AgNO_3$

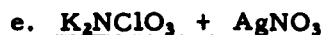#### Material

AgNO$_3$, J. T. Baker Co., Reagent Grade

K_2NClO_3. Prepared as described.

Apparatus

The reactor consisted of a Pyrex glass vessel equipped with a Teflon coated magnetic stirring bar.

Procecure

A solution of AgNO$_3$ was added dropwise to an aqueous solution of K_2NClO_3. A white precipitate was immediately obtained which was dried in a vacuum oven at 50°C. for one hour. Since the silver salt was expected to be very impact sensitive when dry, handling was held to a minimum and there was no attempt to ascertain whether additional heating in vacuo was needed to attain constant weight.

Results

A survey of reactions conducted with K_2NClO_3 and various halogen containing compounds such as ClF_3, NF_2Cl, F_2 and Cl_2 showed that violent explosions generally resulted (68, 89, 90). Our work with K_2NClO_3 confirmed those observations, particularly with ClF_3 which exploded at temperatures as low as -78°C. This prompted a search for new and more applicable intermediates. The compound Ag_2NClO_3 appeared attractive for reaction with NF_2Cl as exemplified by the following equation:

$$2NF_2Cl + Ag_2NClO_3 \xrightarrow{\text{Solvent}} (NF_2)_2NClO_3 + AgCl\downarrow$$

The disilver salt, however, was not known and the first phase of our approach to $(NF_2)_2NClO_3$ was directed toward its preparation.

$$K_2NClO_3 + 2AgNO_3 \xrightarrow{H_2O} Ag_2NClO_3\downarrow + 2KNO_3$$
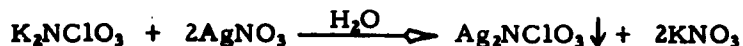
The white precipitate obtained by the proposed reaction was isolated and analyzed.

		Found		Calculated	
		Sample 1	Sample 2	Ag$_2$NClO$_3$	AgNHClO$_3$
Wt. %	Ag	Decomposed	64.1	68.88	52.28
	N	4.23	5.11	4.47	6.79
	Cl	12.2	14.8	11.32	17.18

Elemental analysis of the dried salt showed it to be the desired Ag_2NClO_3 rather than the possible monosilver salt, AgNHClO$_3$.
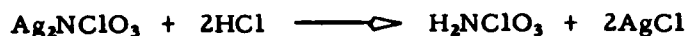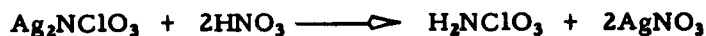
The product undoubtedly contained some impurities and it is expected that anlysis of a purified sample would correspond more precisely to that calculated for Ag_2NClO_3. After this compound had been isolated, a report was received disclosing its preparation independently and simultaneously by this same method by investigators at Dow Chemical Company (89).

The compound Ag_2NClO_3 is soluble in mineral acids and ammonia but insoluble in organic nitrogen compounds such as pyridine, dimethylacetamide acetonitrile, substituted ethanolamines and dicyclohexylamine.

When the freshly precipitated Ag_2NClO_3 was dissolved in nitric acid, a slight residue remained, which was probably silver chloride. This residue was soluble in concentrated hydrochloric acid. Hydrochloric acid solutions of Ag_2NClO_3 liberate iodine from aqueous potassium iodide solution. When Ag_2NClO_3 is added to concentrated sulfuric acid and then stirred, a white residue remains. This residue is insoluble in water but dissolves in concentrated hydrochloric acid. This hydrochloric acid solution does not liberate iodine from potassium iodide solution. These observations may be explained by the following suggested reactions:

$$Ag_2NClO_3 + 2HNO_3 \longrightarrow H_2NClO_3 + 2AgNO_3$$

$$Ag_2NClO_3 + 2HF \longrightarrow H_2NClO_3 + 2AgF$$

$$Ag_2NClO_3 + 2HCl \longrightarrow H_2NClO_3 + 2AgCl$$

$$Ag_2NClO_3 + H_2SO_4 \longrightarrow H_2NClO_3 + Ag_2SO_4$$

It was concluded that the new compound Ag_2NClO_3 had been prepared and an exploratory experiment was immediately conducted in CCl_4 in an attempt to promote the following reaction.

$$2NF_2Cl + Ag_2NClO_3 \xrightarrow{\;CCl_4\;} (NF_2)_2NClO_3 + 2AgCl$$
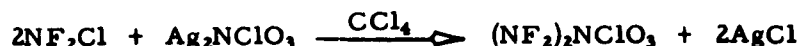
The silver salt, Ag_2NClO_3, was not soluble in the CCl_4 and formed a large pasty mass. Only some decomposition of NF_2Cl occurred.

A search was then instituted for a suitable solvent for this reaction but none could be found.

B. <u>Reactions with $Ba(NHClO_3)_2$, $BaNClO_3$ and NH_2ClO_3</u>

1. <u>Objective</u>

The fluorination of these compounds was considered as a route to the synthesis of new oxidizers. Several of the proposed reactions selected for investigation are exemplified by the following equations.

(a) $$4ClF_3 + BaNHClO_3 \longrightarrow 2ClF_2NHClO_3 + Ba(ClF_4)_2$$

(b) $$4IF_5 + Ba(NHClO_3)_2 \longrightarrow 2IF_4NClO_3 + Ba(IF_6)_2$$

(c) $$NH_2ClO_3 + 2F_2 \longrightarrow NF_2ClO_3 + 2HF$$
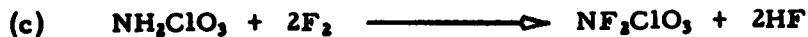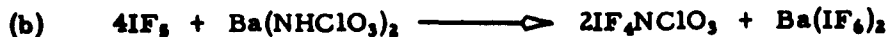
One major difficulty in the use of the two salts $Ba(NHClO_3)_2$ and

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$BaNClO_3$ is their extreme impact sensitivity and the fact that detonations occurred upon addition of fluorine containing reagents to these crystalline solids. However, it was expected that as more experience was gained in the handling of these salts, techniques could be developed to avoid explosions and, in solvent systems, the violent reactions could be controlled to yield new intermediates or candidate solid oxidizers.

The sensitivity of these salts often prevented complete analyses of both the starting materials and the products and, as a result, only limited analytical data was obtained.
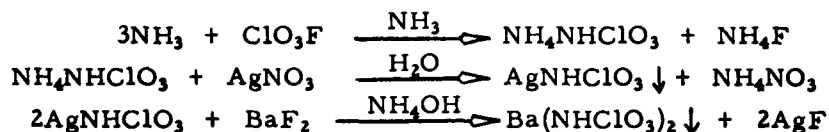
The compound NH_2ClO_3 exists only in solution and even then is prone to decomposition. Fluorination in solution appeared to be a novel approach to the synthesis of NF_2ClO_3, analogous to known fluorination reactions such as the reaction of perchloric acid with fluorine.

$$HClO_4 \quad F_2 \xrightarrow{\quad H_2O \quad} FClO_4 + HF$$
$$NH_2ClO_3 + 2F_2 \xrightarrow{\quad HF \quad} NF_2ClO_3 + 2HF$$
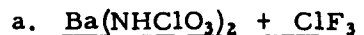
a. $\underline{Ba(NHClO_3)_2 + ClF_3}$

Material

ClF_3, The Matheson Co., Inc. Purity 99%

$Ba(NHClO_3)_2$. Prepared by the method of Englebrecht and Atzwanger (52) by the following reactions:

$$3NH_3 + ClO_3F \xrightarrow{\quad NH_3 \quad} NH_4NHClO_3 + NH_4F$$
$$NH_4NHClO_3 + AgNO_3 \xrightarrow{\quad H_2O \quad} AgNHClO_3 \downarrow + NH_4NO_3$$
$$2AgNHClO_3 + BaF_2 \xrightarrow{\quad NH_4OH \quad} Ba(NHClO_3)_2 \downarrow + 2AgF$$

Pure and dry, $Ba(NHClO_3)_2$ is a very shock sensitive crystalline solid. A sample of this material exploded when a spatula was inserted into the solid powder to obtain a sample for analysis. This material was used as prepared with no analysis.

Apparatus

The Pyrex glass reactor is described in Figure 55. This reactor was attached to a general purpose metal high vacuum.

Procedure

Dry $Ba(NHClO_3)_2$ (0.3 gram) was placed in the Pyrex reactor and the reactor attached to the metal high vacuum line and evacuated. The reactor was then cooled to -78°C. and an excess of ClF_3 (approximately 5 grams) was distilled into the reactor. The reactants were held at 25°C. for 18 hours. The products were then fractionated and analyzed.
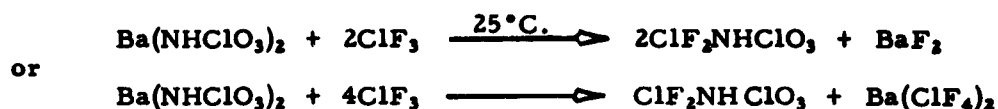
Results

The fluorination of $Ba(NHClO_3)_2$ with chlorine trifluoride was

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investigated to determine whether the compound ClF_2NHClO_3 would form by the following reaction,

or

$$Ba(NHClO_3)_2 + 2ClF_3 \xrightarrow{25°C.} 2ClF_2NHClO_3 + BaF_2$$

$$Ba(NHClO_3)_2 + 4ClF_3 \longrightarrow ClF_2NH\,ClO_3 + Ba(ClF_4)_2$$

A slow reaction occurred at 25°C., resulting in a gradual pressure increase. Analysis of the gaseous product showed high concentrations of SiF_4, apparently formed by interaction of the Pyrex reactor. The recovered solid contained 8.7 weight per cent fluorine but no chlorine.

The results of this experiment were obscured by interaction with the Pyrex reactor and no conclusions could be made on the feasibility of fluorinating $Ba(NHClO_3)_2$ with ClF_3.

b. <u>$Ba(NHClO_3)_2$ + IF_5</u>

Material

IF_5, Allied Chemical and Dye Corp., General Chemical Division.

$Ba(NHClO_3)_2$. Prepared as described.

Apparatus

The Pyrex reactor is described in Figure 55. This reactor was attached to a general purpose metal high vacuum line.

Procedure

Previously dried $Ba(NHClO_3)_2$ (about 0.2 gram) was placed in the reactor and the reactor evacuated. The reactor was then cooled to -78°C. and an excess of IF_5, approximately 5 grams, was distilled into the reactor. The reactants were held at 25°C. for 18 hours. The products and/or reactants were then fractionated and analyzed.

Results

The reaction of $Ba(NHClO_3)_2$ with IF_5 was investigated briefly to determine the feasibility of the reaction:

$$2IF_5 + Ba(NHClO_3)_2 \longrightarrow 2IF_4^+NClO_3^- + Ba^{++}(IF_6^-)_2$$

At 25°C. a slow reaction occurred which resulted in a gradual pressure increase and analysis of the gaseous products showed high concentrations of SiF_4.

Some decomposition of the $Ba(NHClO_3)_2$ apparently occurred. The results of this experiment were generally obscured by interaction of the Pyrex reactor and decomposition of the reactants or products. The use of Pyrex reactors invariably resulted in severe etching of the reactor and formation of SiF_4. Analysis of the resultant solid products was not attempted. The only useful information obtained from this experiment is that this reaction is not vigorous and that an all Teflon system is required.

c. $\underline{BaNClO_3 + HF}$

Material

HF. Merck and Co., Reagent Grade.

$BaNClO_3$. Prepared by

$$NH_4NHClO_3 + Ba(OH)_2 \xrightarrow{H_2O} BaNClO_3 + NH_4OH$$
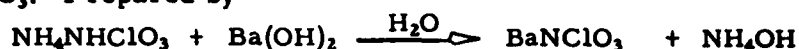
Apparatus

The reactor consisted of a 200-ml. stainless steel vessel which was attached to a general purpose metal high vacuum line.

Procedure

Approximately 0.5 gram of the dried $BaNClO_3$ was added to the reactor and the reactor evacuated and cooled to $-78°C$. Approximately 10 ml. of anhydrous HF was then distilled into the reactor and the reactants were held for several hours at $25°C$.

Results

Condensation of hydrogen fluoride onto the $BaNClO_3$ resulted in solution of the $BaNClO_3$ and the precipitation of a white solid which is apparently the adduct $BaF_2 \cdot HF$. Analysis of this precipitate showed:

	Found	Theory for BaF_2	Theory for $BaF_2 \cdot HF$
Wt. %	27.5	21.67	29.18

Several explosions were experienced when $BaNClO_3$ was cooled to $-196°C$. and the hydrogen fluoride was condensed directly on the salt but when a $-78°C$. bath was used explosions sometimes did not occur. Analysis of volatile gases over the HF solution showed the presence of a trace amount of material whose infrared spectrum conformed to that of N_2O.

On the basis of the formation of BaF_2 and the absence of volatile decomposition products, it appears that the following reaction occurred

$$BaNClO_3 + 2HF \longrightarrow NH_2ClO_3 + BaF_2$$

and the free acid NH_2ClO_3 is stable in HF solution.

The existence of NH_2ClO_3 in solution is further supported by the observations that when K_2NClO_3 is dissolved in HF and the solution is neutralized with aqueous potassium hydroxide, the potassium salt can be regenerated, i.e.,

$$K_2NClO_3 + 2HF \longrightarrow NH_2ClO_3 + 2KF$$
$$NH_2ClO_3 + 2KF + 2KOH \xrightarrow{H_2O} K_2NClO_3 + 2KF + 2H_2O$$
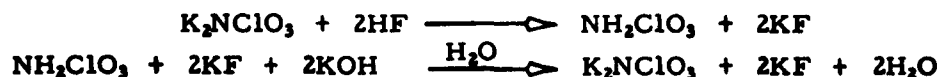
The potassium salt was used for the recovery experiment rather than

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the barium salt because the barium salt is insoluble in water and the neutralization would have been more difficult to control.

Although it appears that the acid can be prepared and is stable in solution, the majority of the attempts to add hydrogen fluoride to the barium salt resulted in explosions. This was particularly true when attempts were made with one gram (or more) quantities of the salt. It is not known whether these explosions were due to initiation of the bulk of the salt by the heat of neutralization or to the sensitivity of the pure acid which may decompose before sufficient hydrogen fluoride has been added. The procedure generally employed was to condense gaseous HF onto the salt contained in a metal reactor. An attempt to pour liquid HF onto the salt also led to an explosion, as did the addition of a small quantity of the salt to liquid HF.

Although stable dilute solutions of NH_2ClO_3 in liquid hydrogen fluoride were prepared, attempts to prepare high concentrations of NH_2ClO_3 in HF by the dissolution of larger amounts of $BaNClO_3$ in liquid HF invariably led to explosions. Apparently the free acid decomposes as it forms, unless stabilized by solution. In the few cases in which the products of decomposition were trapped, N_2O and $NOCl$ were identified.

d. Fluorination of NH_2ClO_3

Material

    F_2. Pennsalt Chemical Corp.

    NH_2ClO_3. Prepared by the following reaction

$$BaNClO_3 + HF \longrightarrow H_2NClO_3 + BaF_2$$
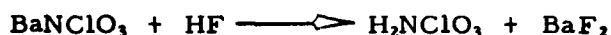
as described in B, 2, c, this section.

    N_2F_4. E. I. DuPont de Nemours and Co., Inc. Purity 99%$^+$.

    HF. Merck and Co. Reagent Grade.

Apparatus

    Generally the reactor consisted of a stainless steel cylinder (approximately 200 ml.) which was attached to a general purpose metal high vacuum line.

Procedure

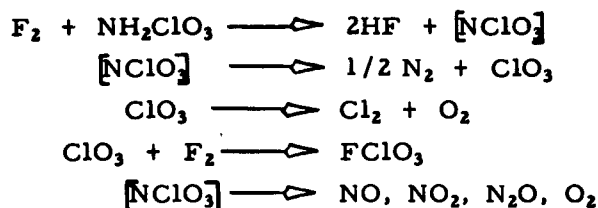   In a typical fluorination, 0.2 gram of dried $BaNClO_3$ is placed in the reactor and the reactor evacuated and cooled to -78°C. Hydrogen fluoride is then distilled into the reactor and the reactants are warmed slowly to 25°C. Fluorine gas or N_2F_4 is then added to the reactor and the reactants are stirred for several hours. The procedure was modified for specific experiments and these changes are noted in the text.

Results

The addition of fluorine to a solution of the barium aminochlorate in hydrogen fluoride was an attempt to prepare NF_2ClO_3

$$NH_2ClO_3 + F_2 \longrightarrow NHFClO_3 \longrightarrow NF_2ClO_3$$

In general, absorption of fluorine did occur but the products appeared to be low molecular weight decomposition products among which were N_2, O_2, NO_2, N_2O, NO and HCl. The only fluorine containing component observed was $FClO_3$. The most probable course of the reaction is one involving abstraction of hydrogen by fluorine, followed by decomposition of the $[NClO_3]$ intermediate. One possible reaction scheme might include the following:

$$F_2 + NH_2ClO_3 \longrightarrow 2HF + [NClO_3]$$
$$[NClO_3] \longrightarrow 1/2\,N_2 + ClO_3$$
$$ClO_3 \longrightarrow Cl_2 + O_2$$
$$ClO_3 + F_2 \longrightarrow FClO_3$$
$$[NClO_3] \longrightarrow NO, NO_2, N_2O, O_2$$

The reaction of N_2F_4 with NH_2ClO_3 in anhydrous HF was investigated as a possible route to the formation of NF hydrazine chlorates, i.e.,

$$N_2F_4 + NH_2ClO_3 \xrightarrow{HF} NF_2H + NF_2 - \overset{H}{\underset{|}{N}} - ClO_3$$
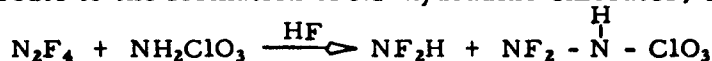
A small amount of NF_2H was found in the volatile products with N_2O, $FClO_3$ and N_2F_4. The presence of NF_2H reflects the possible formation of the desired product. The other products of the reaction, N_2O and $FClO_3$, could have been formed by the decomposition of $NF_2-NHClO_2$ as follows:

$$NF_2\overset{H}{\underset{|}{N}}ClO_3 \longrightarrow FClO_3 + N_2 + HF$$
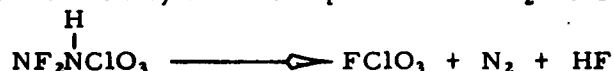
The N_2O could form by oxidation of the aminochlorate since N_2O was also a product from the reaction of fluorine with NH_2ClO_3.

This experiment indicated that the proposed reaction may have occurred but the desired product is not stable, which is in general agreement with numerous experiments designed to produce compounds such as NF_2ClO_3 or NF_2ClO_4.

The limited success with hydrogen fluoride directed our attention to the use of organic solvents. Although water has been considered as a possible reaction medium the probable ease of hydrolysis of the proposed reaction products was a discouraging possibility. Aerojet (91) fluorinated the potassium salt in water and obtained only decomposition products. Attempts were made to extract with ethyl ether, carbon tetrachloride and methylene chloride acidified aqueous solutions of K_2NClO_3. Only in the case of ether could small amounts of material be extracted. The results of these and later experiments were determined by the titer obtained on oxidation of acidified potassium iodide.

One mole of NH_2ClO_3 produces one mole of iodine

$$NH_2ClO_3 + 2HI \longrightarrow I_2$$

Since the distribution ratio for NH_2ClO_3 in water vs. organic solvents was unfavorable for extraction, NH_2ClO_3 was prepared directly in the organic solvent by acidifying a slurry of the salt in the solvent. Methanol appeared to be the most satisfactory solvent and solutions were prepared employing anhydrous hydrogen fluoride as the acid. It is interesting to note that the presence of stoichiometric quantities of acid gave only low values for the amount of NH_2ClO_3 in solution. A three-fold excess of acid produced only 28 per cent of the total titer and a six-fold excess was required to obtain complete solution.

The reaction of N_2F_4 with NH_2ClO_3 in methanol was another attempt to prepare the compound NF_2NHClO_3. A 7 ml. aliquot of the methanol-HF-NH_2ClO_3 solution (0.32 g. NH_2ClO_3) was added to a Monel reactor which then was attached to a metal vacuum line. The reaction vessel was cooled to -196°C. and evacuated before condensing in one gram of tetrafluorohydrazine. The temperature then was raised to -78°C. and the reactor held at this temperature overnight. Samples of the gases were removed for infrared and mass spectrographic examination. The reactor was warmed to room temperature and additional samples taken. Infrared analysis of the volatile products detected NOCl, NO_2, N_2O and N_2F_4. There was no evidence for the presence of the desired compound in the recovered methanol. This experiment was repeated except that the methanol solution was maintained at -78°C. to prevent possible decomposition of unstable products. Similar decomposition occurred and analysis of the products and recovered methanol failed to detect any new N-F compound.

The reaction of fluorine with NH_2ClO_3 in methanol was studied further in a modified apparatus. The reactor was constructed of a Kel-F body with a stainless steel top having an inlet tube that reached to the bottom of the reactor and an outlet tube. The reactor was attached to a copper vacuum line. Twelve ml. of a hydrogen fluoride acidified methanol solution of NH_2ClO_3 (0.36 g.) was added and the system cooled to -78°C. A nitrogen flow of approximately 235 cc./min. was initially bubbled through the solution. The gas flow was then mixed with an additional 20-30 cc./min. of fluorine gas and the mixture passed through the solution for 1.5 hours. The fluorine flow was stopped, the solution flushed with nitrogen and then warmed to room temperature.

Infrared analysis of the gases showed mainly N_2O, NO_2Cl, NO_2F and possibly NO_2 and NF_3. Fractionation of the solution at -130°C. and -75°C. gave several volatile portions whose analyses by mass spectrometry did not indicate the presence of either species containing chlorine bound to oxygen or other chlorine particles. The oxidation titer of the solution decreased to only 6 per cent of the original titer. Distillation of the liquid to dryness did not leave any residue.

Finally, the fluorination of NH_2ClO_3 in water was attempted even though it was doubted that NF_2ClO_3, if formed, would be stable in water. A solution

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of 2.547 g. (14.50 m.moles) of K_2NClO_3 in water was neutralized with 1 N dilute hydrogen fluoride (29.15 m.mole) to gave a total solution of 56 ml. The solution was placed in a glass trap having an inlet tube covered by the solution, and attached to a vacuum line. Fluorine gas, diluted with nitrogen $(10 N_2/F_2)$, was passed through the solution with the exit gases passing through traps at -23°, -78° and -130°C. in series.

Infrared analysis of the effluent gases showed $FClO_3$, N_2O, NO_2 and possibly N_2F_2. An NMR analysis of the fractionated aqueous solution showed no new fluorine peaks and the proton NMR indicated only water.

The reaction solution had only an insignificant remaining oxidation titer. Titration of the solution for ionic chloride showed only 0.5 meq. for the entire solution. The reaction mixture was extracted with methylene chloride, the methylene chloride extracts dried and vacuum distilled to dryness. There was no residue. The aqueous layer was evaporated to dryness and the solid which remained was identified by X-ray as K_2SiF_6.

The reaction of fluorine with aqueous solutions of NH_2ClO_3 apparently leads to complete degradation of the molecule. Evidence for the formation of some $FClO_3$ was obtained, but the preparation of a new oxidizer was not achieved.

The fluorination of NH_2ClO_3 in HF, methanol, or water resulted only in decomposition products. There was some evidence, notably the formation of $FClO_3$, that the desired compound NF_2ClO_3 may have formed, but decomposed at low temperatures even in solution.

The reaction of N_2F_4 with NH_2ClO_3 in HF also indicated that the proposed reaction:

$$N_2F_4 + NH_2ClO_3 \xrightarrow{\text{HF}} NF_2H + NF_2NHClO_3$$
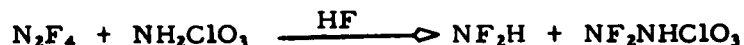
may have occurred since NF_2H was detected in the decomposition products but the desired compound again could not be isolated.

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Section VIII. Reactions with N-Fluorocarbamates

    A. Reactions with $FNHCO_2C_2H_5$ and $KNFCO_2C_2H_5$

        1. Objective

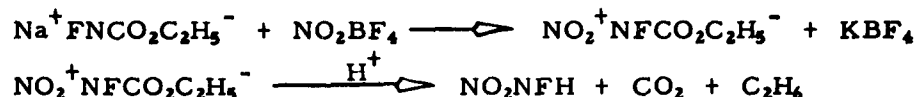A program was initiated to prepare and study the properties of salts of N-fluorocarbamates.

Aerojet (98) described the preparation of N-fluorethylcarbamate by the reaction of fluorine with ethyl carbamate:

$$F_2 + NH_2CO_2C_2H_5 \longrightarrow \overset{H}{\underset{|}{F}}NCO_2C_2H_5 + HF$$

The product was described as a stable liquid, showing an acid reaction in water which could be titrated with base at low temperatures to form the sodium salt:

$$FNHCO_2C_2H_5 + NaOH \xrightarrow{\ H_2O\ } Na^+(FNCO_2C_2H_5)^-$$
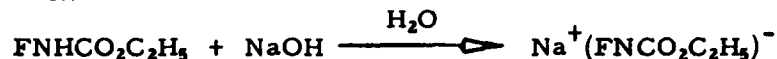
If the dry salt could be isolated it was anticipated that metathesis reactions could be conducted which would lead to the preparation of several new oxidizers, i.e.:

$$Na^+FNCO_2C_2H_5^- + NO_2BF_4 \longrightarrow NO_2^+NFCO_2C_2H_5^- + KBF_4$$

$$NO_2^+NFCO_2C_2H_5^- \xrightarrow{\ H^+\ } NO_2NFH + CO_2 + C_2H_6$$

        a. $FNHCO_2C_2H_5$ + NaOH

Material

$FNHCO_2C_2H_5$, prepared by the following reaction:

$$F_2 + NH_2CO_2C_2H_5 \longrightarrow FNHCO_2C_2H_5$$

Fluorine, 223 g. (5.87 moles) was passed, for a period of 11 hours, through a vigorously stirred solution of 250 g. (2.81 moles) of ethyl carbamate dissolved in 2800 ml. of water contained in a 5-liter round-bottom flask cooled by an ice-salt bath. The solution then was extracted with twenty 300-ml. portions of methylene chloride, the extract dried over $MgSO_4$ and then concentrated to 100 ml. Low pressure distillation with a 50-plate Hasteloy packed column gave 28 grams of product having a purity greater than 97 per cent, based on oxidation titer. The purest fraction, 99.53 per cent, had a refractive index of $n_D^{25} = 1.3941$.

Apparatus

The apparatus generally consisted of standard Pyrex glass laboratory equipment adapted for normal titrations.

Procedure

A number of titrations of the fluorocarbamate with base were conducted followed by acidification to determine whether the sodium salt was stable in solution. Temperatures in the neighborhood of 0 °C. were required to obtain satisfactory oxidation titers and complete decomposition generally resulted at room temperature. Somewhat better titers were obtained if the carbamate was added to the base. In two cases, after neutralization and reacidification, a portion of the solution was extracted with methylene chloride. and analyzed by infrared. The infrared analysis agreed with the oxidation titer indicating that the decomposition products were not capable of oxidizing iodide ion. In general, recoveries in the neighborhood of 60-85 per cent could be obtained if the solutions were kept cold.

Since the sodium salt is reasonably stable in solution when cold, attempts were made to isolate the dry salt and determine its stability. The general procedure employed was as follows: The fluorocarbamate, dissolved in the appropriate solvent, water or methanol, and cooled to 0°C., was added to a solution of sodium hydroxide or sodium methoxide in water or methanol, respectively. In general, a slight excess of base (1 per cent) was used. Poor recoveries generally were obtained when the fluorocarbamate was in excess. The solution at 0°C. was distilled to dryness leaving a yellow oil or white solid. If care is taken to keep the solutions cold throughout the procedure, recoveries above 70 per cent can be achieved.

Results

The sodium salt of ethyl fluorocarbamate was prepared by the following reaction and isolated from aqueous solutions:

$$NaOH + FNHCO_2C_2H_5 \xrightarrow{H_2O} Na^+(FNCO_2C_2H_5)^- + H_2O$$
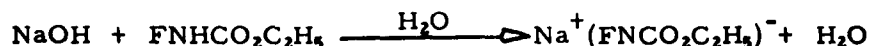
The salt (2.3 m. mole) was added to 10 ml. of solvent held at 0°C. to -10°C. After being shaken, a sample of the solution was titrated for free iodine with standard sodium thiosulfate after the addition of an acidic solution of potassium iodide. The sodium salt was found to be soluble with recoveries of about 80 per cent (based on oxidation titer) in the following solvents: N,N-dimethylformamide, N,N-dimethylacetamide, acetone and a 21 per cent by volume solution of N,N-dimethylacetamide in tetramethylene sulfone. No significant solubility was observed in the following solvents: ethyl ether, acetonitrile, propylene carbonate, nitromethane and dimethylsulfide.

A sample of the sodium salt sputtered and burned after contact with the atmosphere for several seconds. When a cold sample (ca. -10°) was exposed to air at room temperature, it exploded.

The dry sodium salt is stable at 0°C. or lower and decomposes explosively on warming.

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b. $\underline{FNHCO_2C_2H_5 + KOH}$

Apparatus

The apparatus consisted of standard Pyrex glass equipment adapted for normal titrations.

Procedure

A typical procedure is as follows: To an approximately 1.0 N solution of potassium hydroxide or potassium methoxide in methanol cooled to -40°C. is added an equivalent quantity of ethyl N-fluorocarbamate. A white precipitate generally forms. The solution is attached to a vacuum system and the excess methanol removed at -10°C., leaving a white crystalline material. No change in appearance occurs when the solid is warmed to room temperature. The oxidation titer indicates a purity close to 95 per cent. The salt decomposes at 115°C. The salt is soluble in methanol with rapid decomposition under ambient conditions.

Results

The potassium salt of ethyl N-fluorocarbamate was prepared by the following reaction,

$$FNHCO_2C_2H_5 + KOH \xrightarrow{\quad CH_3OH \quad} K^+NFCO_2C_2H_5^- + H_2O$$

and isolated from the solution. The properties of the new salt were investigated.

Sensitivity of Potassium Ethyl N-Fluorocarbamate

Employing the Olin Mathieson Drop Weight Tester no detonation occurred at 28 kg.-cm. A sample did detonate at 50 kg.-cm. Although the material could not be initiated by hammer blows, the sensitivity has not been completely resolved. Two unexplained explosions have been observed with the potassium salt. The first occurred while the pure salt was in an evacuated glass reactor being pumped on. The reactor contained nitronium fluoborate in a side-arm, not in contact with the potassium salt. The second explosion occurred when a small quantity of the salt was being scraped from a sintered glass funnel with a metal spatula. In both cases, samples of the salt were immediately tested in the drop weight tester at 28 kg.-cm and shown to be insensitive.

Thermal Stability

When allowed to stand for 10 days in vacuo under ambient conditions, a sample of the potassium salt developed a yellow color, and showed an oxidation titer which indicated that 65 per cent decomposition had occurred. On the Fisher-Johns melting point apparatus, crystals of the original potassium salt decomposed at 115°C.

Solubility

A sample of the potassium salt was added to approximately 10 ml. of solvent, stirred and permitted to stand for 30 minutes. Where complete solution occurred, an aliquot was titrated with thiosulfate after addition of acidic potassium iodide. For solvents in which complete solution was not observed the mixture was centrifuged and a clear liquid sample removed

and titrated for oxidation titer. Solvents which dissolved the salt with no significant loss in oxidation titer: dimethylacetamide, dimethylformamide and dimethylsulfoxide. Solvents which showed only an insignificant oxidation titer: acetone, nitromethane, acetonitrile, propylene carbonate. In all the insoluble cases, the solid was recovered with little loss of oxidation titer.

Although the salt appeared to dissolve in sulfur dioxide at -10°C., when the solvent was removed after 25 minutes the remaining white solid was observed to have no oxidation titer.

The addition of nitrosyl chloride (containing 10 per cent nitrogen dioxide) to the cold potassium salt caused a violent reaction with the emission of a flash of light.

The potassium salt was soluble in tetramethylene sulfone but decomposed at ambient temperatures as well as at 0°C.

The presence of water in any of the solvents generally increased the rate of decomposition of the potassium salt.

c. $KNFCO_2C_2H_5$ + NO_2BF_4

Apparatus

The reactor consisted of a Pyrex three-neck flask (about 100 ml.) equipped with a Teflon coated magnetic stirring bar. An addition funnel, thermometer and a nitrogen gas inlet were attached to the reactor.

Procedure

All operations were conducted under an inert atmosphere. To a three-neck flask containing a Teflon stirring bar was added 4.59 g. (0.032 mole) of potassium N-fluorocarbamate and 15 ml. of acetonitrile. To the stirred slurry and solvent then was added over a period of 45 minutes a solution of 3.7433 g. (0.028 mole) of nitryl fluoborate in 40 ml. of acetonitrile. The reaction mixture was filtered and the precipitate dried (3.33 g.). Infrared and X-ray examination identified the solid as KBF_4.

An aliquot of the above solution showed that a total of 30.7 meg. of oxidizer was present. The solvent was removed under vacuum leaving a small quantity of orange colored liquid. Vapor phase chromatographic examination showed the presence of three main peaks along with a small fourth peak. The major peak, comprising approximately 50 per cent of the sample, was ethyl N-fluorocarbamate. The second peak was about 10 per cent of the sample and the third peak was about 30 per cent. The fractions were analyzed by infrared and mass spectrometry.

Results

The reaction of the potassium salt with nitryl fluoborate in acetonitrile was investigated as an attempt to prepare the N-fluoro-N-nitro derivative by the following reaction,

$$KNFCO_2C_2H_5 + NO_2BF_4 \xrightarrow{CH_3CN} KBF_4 + NO_2NFCO_2C_2H_5$$

The reaction of the potassium salt with nitryl fluoborate has given

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several interesting results. Greater than 90 per cent of the theoretical amount of KBF_4 could be recovered from the reaction. However, the major product (50%) was the free acid, $NHFCO_2C_2H_5$. It is not known whether the formation of the acid is the result of the presence of trace amounts of water in the system, or occurs by hydrogen abstraction from the acetonitrile solvent. Gas chromatography revealed the presence of three major fractions in the reaction product with the first being identified as $HNFCO_2C_2H_5$. The remaining two fractions along with the starting ethyl N-fluorocarbamate were submitted for examination by mass spectrometry.

The original starting material did not show a peak at its parent mass of 107 mass units. Characteristic peaks, however, were observed at 87 ($N\text{-}COOC_2H_5$), 79(HNF-COOH), 62(HNF-CO) and 59 (N-COOH). Smaller peaks at 93, 92, 91, 72 and 70 were also present in the spectrum of this material; these peaks cannot readily be derived from $HNF\text{-}COOC_2H_5$ and must be due to small amounts of impurities.

The spectrum of fraction "2" reveals prominent peaks at m/e 194, 166, 149, 134, 120, 93, 91, 88, 87, 81, 72, 70, 62, 59, 47, 44, 43, 30 and 29. The peaks at 134, 87 and 81 were especially large.

Fraction "3" generally gave the same peaks as fraction "2". However, fragments at 194, 166 and 149 were missing from this spectrum while those at 47 and 30 were decreased and those at 107, 100, 97, 88, 85, 79, 70 (base peak) and 31 were greatly increased.

It may be stated that the reaction has proceeded to compounds of higher molecular weight than $HNF\text{-}COOC_2H_5$. The mass spectrometric behavior of $NO_2\text{-}NH\text{-}COOC_2H_5$, of course, is unknown; however, judging from the behavior of nitro compounds in general and the fragmentation of the standard sample of $HNF\text{-}COOC_2H_5$, the highest peak which would be expected would be at m/e 106 ($NF\text{-}COOC_2H_5$) or 87 ($N\text{-}COOC_2H_5$). Detection of this compound would thus be impossible as long as it is in the presence of the numerous higher molecular weight compounds which were observed.

The spectrum of fraction "2" shows fragments which could not reasonably arise from a single compound. The highest peak, at 194, would appear to be due to $C_2H_5OCO\text{-}NH\text{-}NF\text{-}COOC_2H_5$, while the peaks at 166 and 149 represent the loss of C_2H_4 and C_2H_5 units from this dimerized molecule. This type of fragmentation parallels that which was observed for the monomer $HNF\text{-}COOC_2H_5$. However, the peak at 134 is incompatible with this structure and the fact that the 134 fragment arises from a different compound is further signified by the spectrum of fraction "3" in which 134 is present but the higher peaks are absent. This 134 fragment could have a number of structural possibilities but it would appear to be $CO\text{-}NF\text{-}COOC_2H_5$ with parent molecules such as $C_2H_5OCO\text{-}NF\text{-}COOC_2H_5$, $FCO\text{-}NF\text{-}COOC_2H_5$, $NO_2NF\text{-}CO\text{-}NF\text{-}COOC_2H_5$ or $HNF\text{-}CO\text{-}NF\text{-}COOC_2H_5$ possibly giving rise to it. The latter two possibilites seem to be especially favorable in view of the fact that a comparison of the spectra reveals that the fragment at 120 arises from the same compound as does the fragment at 134 (no other peak can be so unequivocally related to the 134 peak). The 120 fragment would be N-CO-NF-COOH. The presence of a peak at 70 (CO-N-CO) tends to further

confirm such a structure.

Another very important peak in the spectrum of fraction "2" is the one appearing at m/e 81. Exhaustive consideration of the possibilities reveals very few fragments or molecules which could have this rather unusual mass. About the only reasonable possibilities are: FNO_3, $HN=N-NF_2$, $C_2H_5NF_2$, $(HCN)_3$, $H_5C_4N_2$ or $HNF-COF$. In a complex spectrum such as this, it was not possible to determine whether this peak at 81 was due to a cleavage fragment from some other compound, or whether it, itself, represents yet another component of a mixture.

Many of the other peaks present in the spectrum of fraction "2" are common to too many compounds to be especially descriptive in the case of a mixture. For example, 87 could arise from any molecule having the $N-COOC_2H_5$ arrangement, 62 from any with $HNF-CO$ arrangement, 70 from any molecule with a $CO-N-CO$ or $C-N-COO$ grouping, etc. However, three further points should be mentioned. The absence of a significant peak at 79 indicates the absence of $HNF-COOC_2H_5$ in this second cut. A large peak at 30 indicates the presence of NO or NO_2 compounds of some sort. A fairly large peak at 47 (COF) could lend support to the presence of such a compound as $HNF-COF$.

In fraction "3" no single structure can account for those peaks which were greatly increased. It is undoubtedly a mixture of two or more compounds in addition to the material yielding the 134 peak (the major component, or one of the major components of fraction "2"). The two largest peaks, 70 and 79, would appear to be due to $CO-N-CO$ and $HNF-COOH$ respectively, while a decrease in the peak at 30 reflects a significant decrease in the amount of NO or NO_2 compounds. However, no firm conclusions may be drawn from this spectrum since it is impossible to tell which of the increased peaks belong to one compound and which belong to another.

It may be noted that the large base peak at 70 in fraction "3" corresponds to a small peak in the spectrum of $HNF-COOC_2H_5$. It could well be that the major component in the third cut, or a compound which is structurally similar, is present as an impurity in the starting material. Peaks at 93, 92 and 91 which are derived from a compound (or compounds) also present as an impurity in the starting material are also prominent in the spectra of fraction "2" and "3"; these peaks remain unexplained.

On the basis of the mass spectrometric analysis it appears that one of the products of the reaction is $C_2H_4O_2C-NH-NF-CO_2C_2H_4$ along with other NF and possibly $N-NO_2$ derivatives. The formation of the hydrazine derivative could have resulted from coupling of the potassium salt with the free acid, as shown.

$$C_2H_5O_2CNFK + HNFCO_2C_2H_5 \longrightarrow C_2H_5O_2CNF-NHCO_2C_2H_5 + KF$$
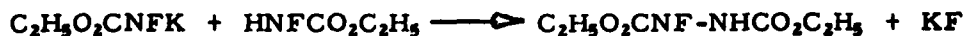
Section IX. Synthesis of Oxyhalogen Fluoride Salts ($M^+ClO_xF_y^-$)

A. Reaction of Various Salts with HF

1. Objective

In 1940, Helmholz and Rogers (99) described the formation of KIO_2F_2 by the reaction of potassium iodate and concentrated hydrogen fluoride and, in 1937, Beck (100) described the formation of K_2ClF_7 by the reaction of potassium chlorate and hydrofluoric acid.

The recrystallization of halates from various concentrations of hydrofluoric acid was investigated as part of a preliminary screening program to determine the feasibility of synthesizing oxyhalogen fluoride salts of the type $M^+ClO_xF_y^-$ and $M^+BrO_xF_y^-$.

a. HF + Metal Salts

Material

$KBrO_3$, $NaBrO_3$ ⎤
$KClO_4$, $Mg(ClO_4)_2$ ⎟   Fisher Scientific Co. , Reagent Grade.
$NaClO_4$, $KClO_4$ ⎦

KIO_3, $KClO_3$. Mallinckrodt Chemical Works, Analytical Reagent

$LiClO_3$, $LiClO_4$. American Potash and Chemical Corp.

$NaClO_3$. J. T. Baker Chemical Co. , Reagent Grade.

$AgBrO_3$, NH_4ClO_4. Matheson, Coleman and Bell, Reagent Grade

HF. Merck and Co. , Inc.

Apparatus

The apparatus consisted of an open polyethylene beaker equipped with a Teflon coated magnetic stirring bar.

Procedure

In the attempted formation of oxyhalogen fluoride compounds, an ionic bromate, chlorate, or perchlorate salt was dissolved (with heating and stirring) in aqueous hydrofluoric acid, made up to a specific concentration. The crystals were usually collected after standing for 24 hours, by decantation of the liquid phase. The recovered moist salt was then placed in a vacuum desiccator and dried over a 24-hour period under vacuum. A sample of the dried salt was then analyzed for fluorine, chlorine, or bromine content and X-ray analyses were done.

Results

The purpose of this investigation was to determine whether a reaction occurs between various salts and hydrofluoric acid to form oxyhalogen fluorides, i. e.,

$$2NaClO_3 + HF \longrightarrow Na_2ClO_3F + HClO_3$$

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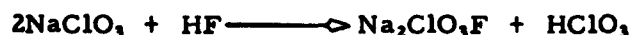
If a reaction occurred at all, it was anticipated that the following reaction would occur rather than the formation of an oxyhalogen fluoride:

$$NaClO_3 + HF \longrightarrow NaF + HClO_3$$

The results of a series of experiments are summarized in Tables 91 and 92.

The bromate salts undergo some decomposition in aqueous HF with loss of elemental bromine. In general, it was found that the products recovered from the HF solutions contain only small amounts of fluorine. The product obtained by recrystallization of sodium chlorate from hydrofluoric acid, however, exhibited a high fluorine content in contrast to the reaction product from potassium chlorate and hydrofluoric acid.

X-ray diffraction studies of the product from the reaction of potassium chlorate and HF showed that the substance consisted of a mixture of potassium fluoride and unreacted potassium chlorate. There was no evidence throughout this study that supported the work of Beck (100) who isolated a compound having an empirical formula $K_2ClF_7(KClF_6 \cdot KF)$ by this reaction.

Further, there was no evidence for the formation of salts containing oxyhalogen fluoride anions in any of the other products from the reactions described in Tables 91 and 92. The high fluorine content of the products obtained by the reaction of sodium chlorate and hydrofluoric acid can be accounted for by a mixture of NaF and $NaF \cdot HF$.

Based on the formation of metal fluorides in this study, it appears that the following reactions occurred

$$KClO_3 + HF \longrightarrow KF + HClO_3$$
$$NaClO_3 + HF \longrightarrow NaF + HClO_3$$
$$KBrO_3 + HF \longrightarrow KF + HBrO_3$$
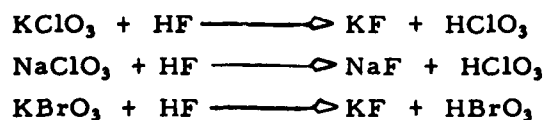
and decomposition of the unstable acids $HClO_3$ and $HBrO_3$ would result in a mixture of metal fluorides and unreacted metal chlorates or bromates.

This is analogous to the reaction of $BaNClO_3$ with HF when the following reaction occurred.

$$BaNClO_3 + HF \longrightarrow BaF_2 \downarrow + NH_2ClO_3$$

This reaction is discussed in Section VII, B, 1, b.

B. Reactions with Transition Metal Fluorides

1. Objective

In 1956, Mitra and Ray (56) postulated the formation of an oxyfluoride anion of chlorine (ClO_3F^{2-}) and the preparation of soluble

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NH-2090

Table 91

Recrystallization of Halate Salts from HF

Expt. No.	Salt	Concentration Of HF (per cent)	Solution Temperature (°C)	Analysis		Remarks
				Per Cent Chlorine Bromine or Iodine	Per Cent Fluorine	
1862D- 7	$KBrO_3$	24	50-60	43.0 ± 0.1	5.85 ± 0.05	Evidence of decomposition Red bromine color developed.
8	$NaClO_3$	24	50-60	7.34 ± 0.13	46.4 ± 0.2	
9	$NaBrO_3$	24	50-60	5.00 ± 0.10	18.4 ± 0.1	Evidence of decomposition bromine evolved.
10	KIO_3	48	50-60	64.4 ± 0.2	15.4 ± 0.1	
11	$KClO_4$	36	50-60	25.0 ± 0.1	1.60 ± 0.17	
12	$KClO_3$	24	50-60	27.5 ± 0.0	2.57 ± 0.22	
13a	$Mg(ClO_4)_2$	36	50-60	-	-	Insol. MgF_2 formed
13b	$AgBrO_3$	36	50-60	-	-	$AgBrO_3$ insol. &.q . HF
13c	$LiClO_3$	24	warmed slightly	-	-	LiF formed
13d	$LiClO_4$	24	warmed slightly	-	-	LiF formed
14	NH_4ClO_4	36	50-60	29.8 ± 0.2	0.36	
15	$NaClO_4$	36	50-60	6.8 ± 0.2	44.8 ± 0.5	
16	$KClO_3$	48	60	27.1 ± 0.2	2.2 ± 0.1	Crystals in contact with HF for one week.
17	$KClO_4$	48	80-85	26.2 ± 0.2	0.77	Heated for three hours at 80 - 85°.
18	$KClO_3$	48	70-75	27.5 ± 0.0	2.0 ± 0.1	Heated for two hours at 70 - 75°.

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Table 92

Recrystallization of Halate Salts from Hydrofluoric Acid

Experiment Number	Salt	HF Concentration	Solution Temp. °C	Analysis		Remarks
				Per Cent Cl	Per Cent F	
1862D-19A	KClO$_3$	48%	80-85°	24.5	7.1	Solution treated for 2 hours. Crystals on cooling were redissolved in 48% HF and heated for 3 hours at 80-85°.
1862D-19B	Residue from first recrystallization after evaporation of solution to dryness.			24.1	2.2	
1862D-19C	Residue from second recrystallization after evaporation of solution to dryness			26.9	3.7	
1862D-21A	NaClO$_3$	24%	50-60	1.3	54.6	Solution heated for 1 hour. High F% can be accounted for by mixture of NaF and NaHF$_2$.
1862D-21B	NaClO$_3$	48%	60-70	8.4	42.8	Solution heated for 2 hours.

transition metal salts containing this ion was described. At a later date, these investigators reported the formation of a fluoroiodate anion ($IO_3F^=$) (101). These, together with the oxydifluoroiodate anion (IO_2F_2) reported by Helmholz and Rogers (99) are the only cases of fluorohalate ions that could be found in the literature.
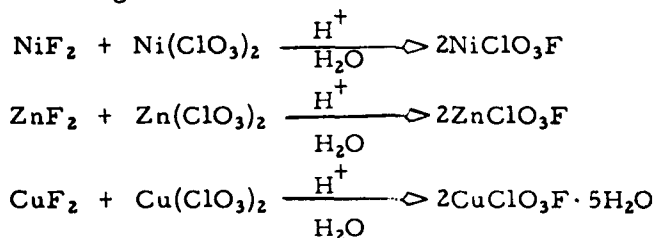
Compounds containing ions of this type, especially the fluorochlorate anion, were of obvious interest to us for application to the synthesis of solid oxidizers and a study of these reactions was initiated to determine the feasibility of incorporating the application of these compounds in our research program.

The preparation of transition metal oxyfluorochlorate salts was investigated.

a. Transition Metal Oxyfluorochlorates

The results of more than fifty experiments are summarized in Tables 93, 94 and 95.

Most of the experiments were designed to duplicate the work of Mitra and Ray (56) who prepared the oxyfluorochlorate salts of nickel, zinc and copper by the following reactions:

$$NiF_2 \ + \ Ni(ClO_3)_2 \ \xrightarrow[\ H_2O\ ]{\ H^+\ } \ 2NiClO_3F$$

$$ZnF_2 \ + \ Zn(ClO_3)_2 \ \xrightarrow[\ H_2O\ ]{\ H^+\ } \ 2ZnClO_3F$$

$$CuF_2 \ + \ Cu(ClO_3)_2 \ \xrightarrow[\ H_2O\ ]{\ H^+\ } \ 2CuClO_3F \cdot 5H_2O$$

In experiment 18620-23, Table 93, when nickel fluoride was reacted with nickel chlorate in an aqueous acidic medium, the recovered product also gave an approximate elemental composition for $NiClO_3F \cdot 6H_2O$, however, the fluorine was mostly ionic and there was no evidence for the presence of covalently bonded fluorine by NMR or infrared analyses. In most cases, the recovered products of the many experiments consisted of a mixture of metal fluorides and the corresponding metal chlorates. Our inability to produce the results of Mitra and Ray prompted us to discontinue this work early in 1960. Prior to this, however, we contacted both Mitra and Ray, who was then at New York University, along with Drs. P. F. Winternitz and A. A. Carotti. All of these workers confirmed the preparation of the oxyfluorochlorate salts of barium, copper, nickel and zinc (102).

At the time of the writing of this report (1963), it now appears that Pennsalt Chemicals has confirmed our early results (104). While materials prepared by Pennsalt had elemental compositions approximating the oxyfluorochlorate salts, they were shown to be mixtures of the simple metal chlorate and fluoride salts. On the other hand, in a paper delivered at the First Propellant Contractors' Synthesis Conference in New York on

Table 93

Attempted Preparation of Fluorochlorates

Experiment Number	Molar Reactants		Molar Ratio	Reaction Temp. °C.	Time (min)	Product Analysis			Comments
						Cl	Total F	Ionic F	
1862D-23	NiF_2 0.0078	$Ni(ClO_3)_2 \cdot 6H_2O$ 0.0090	Approx. 1/1	80-85	30	21.1	5.38	4.38	Total fluorine low. Ionic fluorine high.
1862D-27	MgF_2 0.02	$Mg(ClO_3)_2 \cdot 6H_2O$ 0.02	1/1	80-85	30-40	21.44	8.33	0.17	Total fluorine low.
1862D-24	BaF_2 0.02	$Ba(ClO_3)_2 \cdot H_2O$ 0.02	1/1	80-85	60	No analysis			Incomplete digestion.
1862D-26	CaF_2 0.02	$Ca(ClO_3)_2 \cdot 2H_2O$ 0.02	1/1	80-85	60	No analysis			Incomplete digestion.
1862D-28	NiF_2 0.05	$Ni(ClO_3)_2 \cdot 6H_2O$ 0.05	1/1	80-85	60	17.84	2.01	1.77	Low total fluorine due in part to water of hydration assoc. with NiF_2.
1862D-29	MgF_2 0.05	$Mg(ClO_3)_2 \cdot 4H_2O$ 0.05	1/1	80-85	120	21.3	10.1	0.24	Fluorine 1.5% low for desired product: $MgClO_3F \cdot 2H_2O$.
1862D-32	NiF_2 0.05	$Ni(ClO_3)_2 \cdot 6H_2O$ 0.05	1/1	80-85	245	No chemical analysis. NMR failed to detect ionic fluorine.			
1862D-33	NiF_2 0.025	$Ni(ClO_3)_2 \cdot 6H_2O$ 0.025	1/1	80-85	60	13.8	5.15	5.02	Total fluorine 2% low for desired product: $NiClO_3F \cdot 6H_2O$.

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Table 94

ATTEMPTED PREPARATION AND IDENTIFICATION OF FLUOROCHLORATES

Experiment Number	Molar Reactants	Acidic Medium	Reaction Temp. °C	Time (min.)	Product Analysis	Comments
1062D-34	Approx. 3 g. of $NiF_2 \cdot 4H_2O$ in 50 ml. H_2O at 85°C.				NMR	No signal for F Concentration too weak
-35	$NiF_2 \cdot 4H_2O$ $Ni(ClO_3)_2 \cdot 6H_2O$ 0.0125 0.0125	CH_3COOH	80-85 16 hr	40 Room Temp.	NMR U.V.	No signal. Compared with NiF_2 + $Ni(ClO_3)_2$ standards. Main peak in all 3 solutions at 3990 cm^{-1} due to Ni^{2+}. UV as on Ni^{2+} solutions with various $[F^-]$ was attempted to gain possible evidence of Ni-F bond. No tangible results were obtained
-36	MgF_2 $Mg(ClO_3)_2 \cdot 4H_2O$ 0.025 0.025	HNO_3	80-85	65	U.V.	No bands indicative of either Mg-F or Cl-F bonding
-40	Approx. 0.05 moles of MgF_2 in 50 ml. of water	HNO_3	80-85	45	Mg 21.2% F 41.2%	Results indicate loss of fluorine thru H-F formation when solution is evaporated to dryness
-41	0.02 moles of $NiF_2 \cdot 4H_2O$ in 50 ml. of water	HNO_3	80-85	60	Ni 51.7% F 12.0%	See above remarks.
-42	Approx. 0.05 moles of ZnF_2 in 60 ml. of water	HNO_3	80-85	90	Zn 31.2% F 9.11%	See above remarks. ZnF_2 sample was later analyzed and found impure.
-43	0.025 moles of MgF_2 in 72 ml. of 2.0 N HNO_3		80-85	60	Titration with 2N NaOH	No change in $[H^+]$
-44	BaF_2 $Ba(ClO_3)_2$ 0.02 0.02	HNO_3	80-85	90	Cl 0.51% F 0.10%	Product was $Ba(NO_3)_2$.
-46A	MgF_2 $Mg(ClO_3)_2 \cdot 4H_2O$ 0.05 0.05	HNO_3	80-85	90	I.R. - KBr pellet	Only ClO_3^-, NO_3^-, and H_2O bands were observed.
-46B	Addition of Ba^{++} to above solution				I.R. - KBr pellet	Only NO_3^- bands were observed.
-47	$NiF_2 \cdot 4H_2O$ $Ni(ClO_3)_2 \cdot 6H_2O$ 0.025 0.025	CH_3COOH	80-85	60	Cl-negative F-22.1% I.R. KBr pellet	Precipitate on cooling was primarily NiF_2. Similar to IR spectrum of starting reagent.
-49	$NiF_2 \cdot 4H_2O$ $Ni(ClO_3)_2 \cdot 6H_2O$ 0.0125 0.0125	HNO_3	80-85	60		
-49A	Ba^{++} + above solution				I.R.	Slight ClO_3^- band, broad band 13-14.5μ.
-50	1062D-49 solution tested with Pb				I.R. KBr-pellet	No dominant bands. Results not conclusive.
-51	1 mg. each of BaF_2 + $Ba(ClO_3)_2$ mixed with 500 mg. KBr.				I.R.	Only ClO_3^- and H_2O bands observed.
-52	1/1 molar ratio of BaF_2 to $Ba(ClO_3)_2 \cdot H_2O$ in 2 mg. sample made into pellet with 500 mg. of KBr.				I.R.	Only ClO_3^- and H_2O bands observed.
-54	1/1 molar ratio of $NiF_2 \cdot 4H_2O$ to $Ni(ClO_3)_2 \cdot 6H_2O$ in 2 mg. sample made into pellet with 500 mg. of KBr.				I.R.	Only ClO_3^- and H_2O bands observed.
-55	Approx. 3.4 g. of KIO_3 recrystallized from hot 48% HF solution.				I.R. - KBr pellet	Conversion of IO_3^- to $IO_2F_2^-$. Main band shift from 13.25 to 13.2μ.
-56A	$NH(OH)_2$ NiF_2 HNO_3 0.02 0.02 0.04	CH_3COOH	80-85	90	I.R. - KBr pellet	Incomplete solution of $NH(OH)_2$ and NiF_2. Evaporation of solution to dryness. Product gave inconclusive spectrum.
-56A	ZnF_2 $Zn(OH)_2$ HNO_3 .05 .05 0.10	CH_3COOH	80-85	45	I.R. - Nujol mull	Incomplete solution of reactants. Undissolved solid gave IR band at 13μ (probably IO_3^-).
-56B	Residue from evaporation of -56A filtrate				Cl 14.13% F 7.73% Zn 24.1%	Product is probably a mixture.
-59A	$NiF_2 \cdot 4H_2O$ $Ni(ClO_3)_2$ soln. 0.02 0.02	12% HF soln.	80-85	60	I.R. - KBr pellet	Strong unknown band at 13-14μ region. Weak ClO_3^-. Large H_2O bands.
-59B	Above solution + Ba^{++}				R. - KBr pellet	White product gave strong 13-14μ band. Low in H_2O.
-62A	$NiF_2 \cdot 4H_2O$ $Ni(ClO_3)_2$ soln. 0.045 0.045	12% HF soln.	80-85	60	I.R. - KBr pellet	ClO_3^- band, H_2O, and unknown 13.5μ band.
-62B	Above soln. + Ba^{++}				I.R. Nujol mull Cl 4.1%, F 20.5, Ba 46.9	Unknown doublet at 8.5μ and 8.75μ. Possibly BaF_2 HF with impurities.
-62C	Evaporated soln. from -62A + Ba				I.R. - KBr pellet	Unknown doublet at 8.5μ, H_2O, traces of unknown at 13.75 and 14μ.
-62D	Ni salt from -62A dissolved in H_2O and treated with Ba				Cl 0%, variable F 16-17%, 47.0% Ba I.R. - Nujol mull	Possibly $BaNiF_4$. Broad 13.7μ band.
-65A	ZnF_2 $Ba(ClO_3)_2 \cdot 2H_2O$ 0.09 0.09	HNO_3	80-85	90	I.R. - Nujol mull Cl 4.19% F 29.0%	Flattened ClO_3^- band at 10-11μ. Mixture of ZnF_2 and trace ClO_3^-.
-65B	2nd crystal crop from -65A				I.R. - Nujol mull	Broad ClO_3^- band, NO_3^-, H_2O
-67A	$NiF_2 \cdot 4H_2O$ $Ni(ClO_3)_2$ 0.09 0.09	HNO_3	80-85	90	I.R. - Smear	Primarily ClO_3^- band. Also broad unknown band at 13.75μ.
-67B	Nickel salt from -67A dissolved in H_2O and treated with Ba				I.R. - Nujol mull	NO_3^- bands. Also broad 13.5μ spectrum.
-67C	Soln. from -67A treated with Ba				I.R. - Nujol mull	Primarily $Ba(NO_3)_2$.
-68A	NiF_2 $Ni(ClO_3)_2$ sol. .01 .01	None	80-85	60	I.R. - Nujol mull	Addition of N HNO_3 to NiF_2 solution produced precipitate whose IR spectrum was negative.
-68B	Initial crystal crop from -68A				I.R. - Nujol mull	Trace of ClO_3^- band.
-68C	2nd crop from -68A				I.R. - Smear	Definite ClO_3^- band.
-68D	Ba^{++} + solution from -68C				I.R. - Nujol mull	No definite spectrum.

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Table 95

Attempted Preparation and Identification of Fluorochlorates

Experiment Number	Molar Reactants		Medium	Reaction Temp. °C	Time (min)	Product Analysis	Comments
1862D-72	NiF₂·4H₂O .05	Ni(ClO₃)₂ .05	CH₃COOH	80-85	120	Mainly NiF₂. Only 6.11% chlorine in product	IR bands indefinite. Only a trace of chlorate structure. Microscopic examination inconclusive.
73	NiF₂·4H₂O .05	Ni(ClO₃)₂ .05	HNO₃	80-85	120	Mainly NiF₂. Only 6.07% chlorine in product	IR bands indefinite. Only a trace of chlorate structure. Microscopic examination inconclusive.
82	ZnF₂ .05	Zn(ClO₃)₂ .05	CH₃COOH	80-85	120	Zn 55.15%, Cl 2.87%, F 27.47%.	Product is primarily ZnF₂ with a trace of Zn(ClO₃)₂.
83	NiF₂·4H₂O .05	Ni(ClO₃)₂ .05	CH₃COOH	80-85	120	Ni 32.1%, Cl 0.74%, F 22.4%.	Product is primarily NiF₂
84	NaHCO₃ .05 / Excess Cl₂	NaF .025	Aqueous	Room		Ionic F 0.68 Total F 0.70	Aliquot of solution was analyzed
85	Na₂CO₃ .05 / Excess Cl₂	NaF .025	"	80-90		Ionic F 0.57 Total F 0.60	Solid residue after evaporation gave evidence for chlorate bands in infrared
86	NaOH .05 / Excess Cl₂	NaF .025	"	80-90		Ionic F 0.35 Total F 0.38	Aliquot of solution analyzed
87	ZnO .02 / Excess Cl₂	ZnF₂ .01	"	80-90		Ionic F 0.90 Total F 0.99	Aliquot of solution analyzed
88	ZnO .04 / Excess Cl₂	KF .02	"	Room		Ionic F 0.39 Total F 0.42	Aliquot of solution analyzed
89	ZnO .04 / Excess Cl₂	KF .02	"	80-90		Zn 4.93%, Total Ionic F 0.22 Cl 4.59% Total F 0.34	Further investigation necessary to determine source of covalent fluorine.
90	MgO .04 / Excess Cl₂	KF .02	"	80-90		Mg 1.32% Total Ionic F 0.19 Cl 3.76% Total F 0.33	Further investigation necessary to determine source of covalent fluorine.
91-A	Ba(OH)₂ .02 / Excess Cl₂	BaF₂ .01	"	80-90		Ba 71.2% Total Cl 16.8% Total F 11.0%	Analysis of solids remaining after reaction. Further investigation necessary.
91-B	Above solution		"			Total F negative Ionic F	
92	Ba(OH)₂ .02 / Excess Cl₂	KF .01	"	80-90		Total F negative Ionic F	Solids after reaction not analyzed. Investigation is continuing.

April 16, 1963, A. A. Carotti reaffirmed the preparation and existence
of the salts in question (105). Consequently, it must be concluded at this
time that there exist differences of opinion which, it is hoped, can be
shortly resolved.

Section X. **Synthesis and Some Properties of Intermediates**

A. **Objective**

During the course of this program it became necessary to synthesize various reagents and intermediates. In so doing, information of both a preparative and chemical nature was obtained. With respect to the latter, it was expected that as our knowledge of a particular reagent became more complete we would be able to use this information for the fullfilment of the ultimate objectives of the program.

This section contains information on the compounds NF_2H, NF_2Cl, $FOClO_3$, Cl_2O_6 and N_2F_4.

1. **Synthesis of NF_2H**

The preparation of NF_2H from N_2F_4 and thiophenol, $\emptyset SH$, is based on the following reaction:

$$N_2F_4 \; + \; 2\emptyset SH \xrightarrow{\;50°C.\;} 2NF_2H \; + \; \emptyset S - S\emptyset$$

Yields of 70-78% of high purity NF_2H have been achieved by this method using a cycling system (23). Initial reactions with fresh $\emptyset SH$ usually result in low yields. Subsequent experiments with the same $\emptyset SH$ solution lead to higher yields.

Experimental

a. **Materials**

N_2F_4. E. I. duPont, 99% pure.

Thiophenol. Pitt-Consol Chemical Co., 98% pure.

b. **Apparatus**

A drawing of the cycling apparatus used in the N_2F_4-$\emptyset SH$ preparation of NF_2H is shown in Figure 56.

c. **Procedure**

In a typical experiment, 250-300 ml. of $\emptyset SH$ is cooled to 0°C. with an ice bath and the system evacuated to remove the nitrogen atmosphere above the solution. At this temperature the system is successfully evacuated without distilling off any significant amount of $\emptyset SH$, which would occur if the solution were at room temperature. At 0°C., N_2F_4 is slowly added to the $\emptyset SH$ solution to a pressure of 600 mm. Hg. Under this pressure N_2F_4 will be above its boiling point at -78°C. and will not condense along with NF_2H in the collection trap at -78°C. Under this maximum allowable pressure of 600 mm. the bellows pump will function at its highest possible efficiency.

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Figure 56   Preparation of NF₂H

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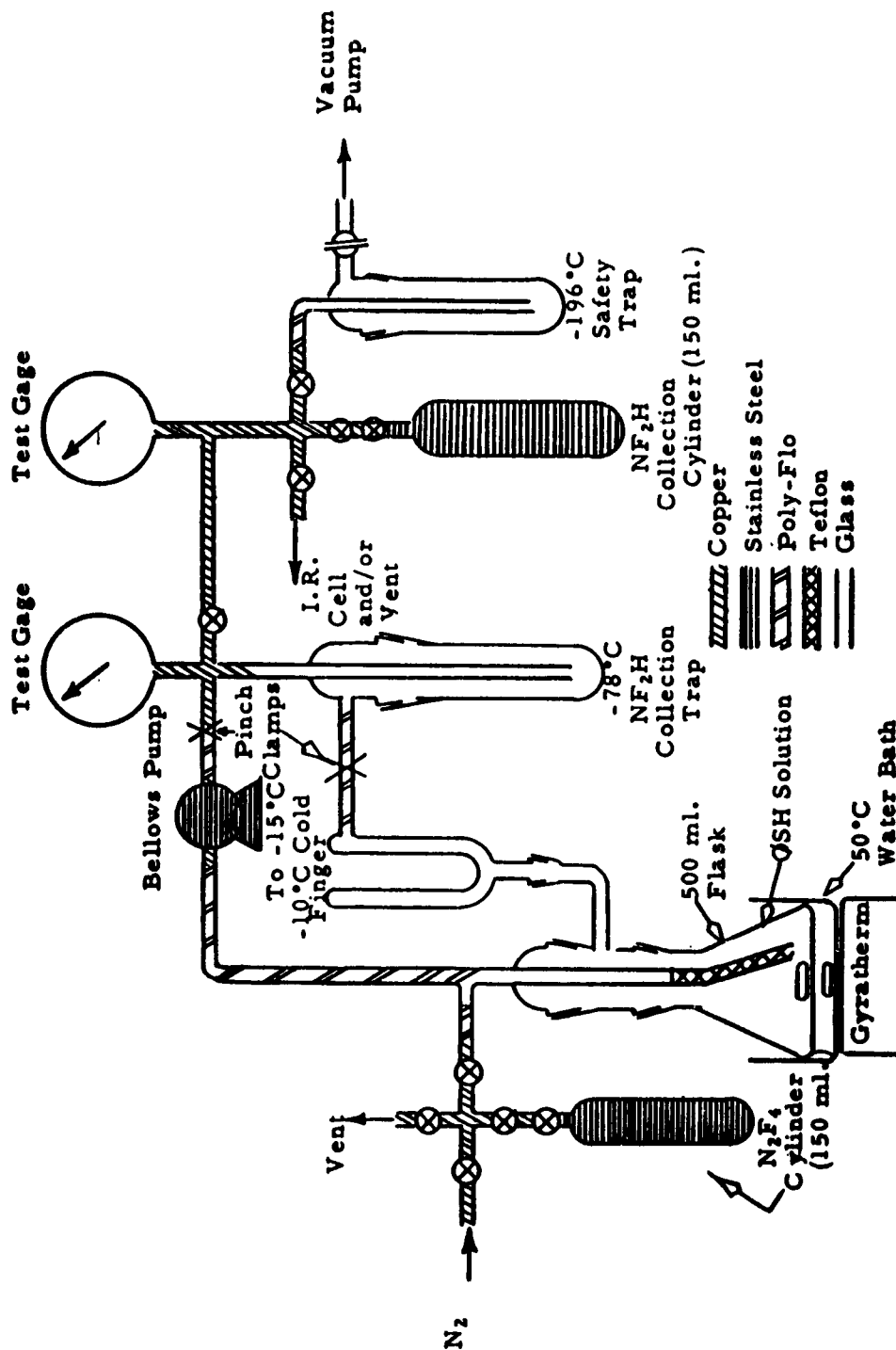
After addition of N_2F_4, the ice bath around the $\emptyset$SH solution is replaced with a water bath which is then warmed to the reaction temperature of 50°C. Rapid stirring of the $\emptyset$SH is accomplished with a magnetic stirring bar. The N_2F_4 is cycled through the $\emptyset$SH solution, then through the -10° to -15°C. cold finger trap. This trap tends to condense out $\emptyset$SH vapors before they reach the trap at -78°C. where the NF_2H is collected as a liquid. The N_2F_4 then is recycled through the bellows pump back to the reaction flask containing the $\emptyset$SH solution.

As the N_2F_4 reacts with $\emptyset$SH to generate NF_2H the system pressure is allowed to decrease to 575 mm. At this point more N_2F_4 from the supply cylinder is added and the pressure of the system returned to 600 mm. When all the N_2F_4 from the supply cylinder has been added, dry nitrogen is introduced to maintain the system pressure at 600 mm.

The reaction is terminated normally after 3-5 hours and the color-less NF_2H liquid is transferred to a pre-cleaned, metal fluoride free, stainless steel cylinder at -78°C. Traces of white and light yellow solids (N_2O_4 and/or $\emptyset$SH or $\emptyset$S-S$\emptyset$) floating in the liquid NF_2H at -78°C. remain behind as the NF_2H distills into the cylinder. The cylinder containing the liquid NF_2H at -78°C. finally is evacuated quickly to remove any volatile gases above the liquid.

The cycling system then is pressured to atmospheric pressure with dry nitrogen and allowed to stand until the next reaction is run. The NF_2H cylinder is weighed and samples of the gas submitted for infrared and mass spectrometric analyses. Figure 57 is a reproduction of the infrared spectrum.

As part of a continuing study of the reactions of NF-intermediates, it was necessary to search for reaction media which would prevent or minimize the explosive reactions which generally occur. In addition, it was considered desirable to effect many proposed reactions in media of high dielectric constant which would offer the possibility of heterolytic bond cleavage for the reaction path. The solubility of difluoramine, therefore, was examined in hydrogen fluoride and in sulfur dioxide.

The solvent was condensed into a trap attached to a vacuum line and maintained at -78°C. A known quantity of gaseous difluoramine then was slowly added. The vapor pressure of the solution was determined at various temperatures, and the overhead gases were analyzed by infrared spectroscopy.

1. <u>Hydrogen Fluoride</u> - On the addition of the first few milliliters of gaseous difluoramine to liquid hydrogen fluoride at -78°C., a number of small flashes and explosions were observed. Further addition of difluoramine proceded smoothly. Infrared analysis of the overhead gases showed the absence of difluoramine and the presence of N_2F_4. The N_2F_4 appeared to be soluble in the HF since the vapor pressure of the solution was only slightly above that for pure HF.

Figure 57: Infrared Spectrum of NF_2H
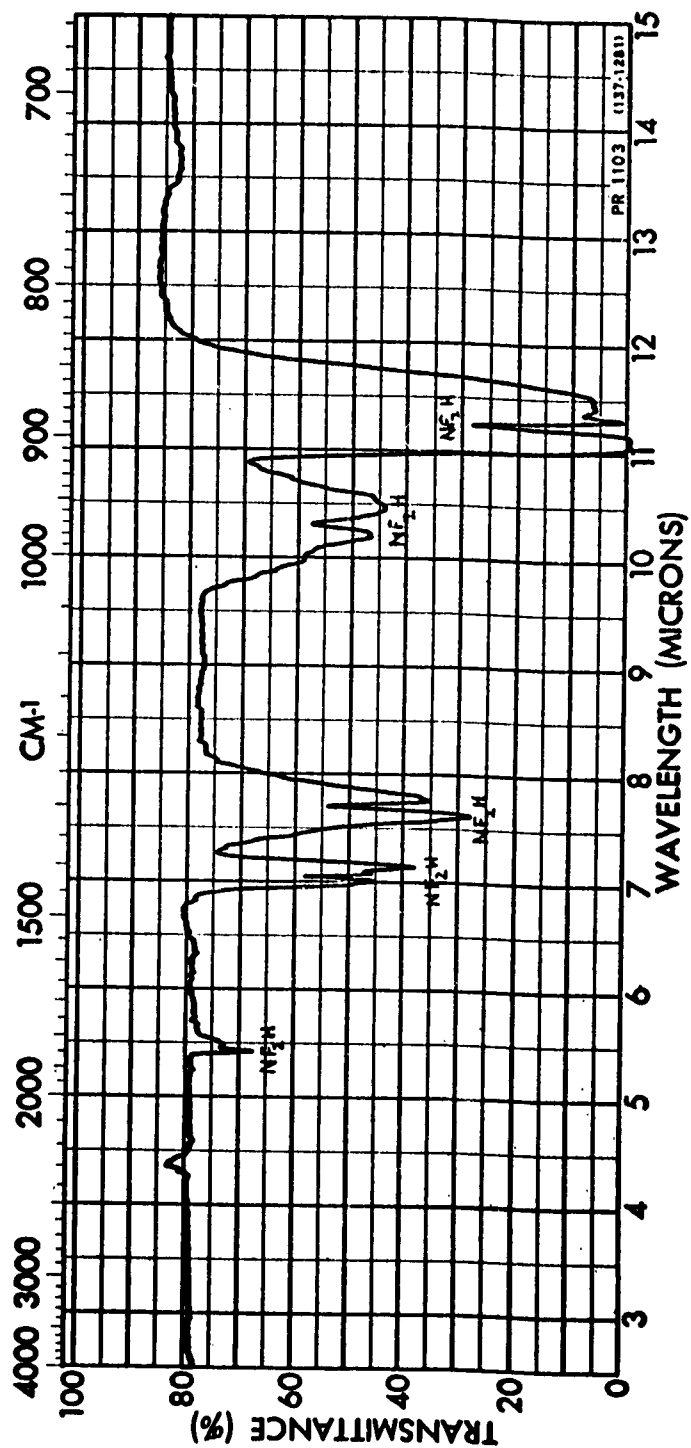
2. <u>Sulfur Dioxide</u> - Difluoramine was found to be compatible and soluble in sulfur dioxide. No attempt was made to obtain the maximum solubility but 0.15 g. easily dissolved in 30 ml. of sulfur dioxide. No significant vapor concentration of difluoramine could be detected above the solution at -78°C, -55°C. or at -30°C., when analyzed by infrared. As the boiling point of sulfur dioxide (-10°C.) was approached, the concentration of difluoramine in the vapor increased.

2. Preparation of NF_2Cl

The preparation of NF_2Cl is based on the following reaction:

$$NF_2H + NaOCl \xrightarrow{H_2O} NF_2Cl + NaOH$$
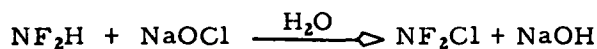
After studying a wide range of variables, particularly with respect to the preparation of the hypochlorite solution, the method described below was employed. The procedure is very similar to that employed by the Callery Chemical Co. and we are grateful to Dr. Marshall of Callery for helpful suggestions (92).

Experimental

a. Reagents

$NF_2H(99-100\%)$. Prepared by the $N_2F_4-\emptyset SH$ method.

Cl_2. Matheson Co.

NaOH. Mallinckrodt (Analytical Reagent)

b. Apparatus

The apparatus employed is shown in Figure 61.

c. Procedure

The "hypochlorite" solution was prepared in the following manner: To 190 ml. of distilled water is added 10 g. of NaOH and the resulting solution stirred. An ice bath is placed around the solution and chlorine bubbled through a fritted tube into the stirred solution. After about 15 minutes the clear solution turns yellow-green and yellow foam appears on the surface. A light flocculent precipitate usually appears at this point and the chlorination is continued at a moderate rate for about another 15 minutes. Finally, the solution is decanted and found to have a pH of 4 to 5.

A 100 -ml. aliquot of this solution is placed in the reaction column which is cooled to 0°C. in an ice bath. The system is flushed for 10-15 minutes with dry nitrogen to remove air. The valve to the vacuum is regulated to maintain the system pressure at 15'' vacuum (375-400 mm.) and NF_2H allowed to bubble through the solution. As the NF_2H passes

Figure 61: Preparation of NF_2Cl
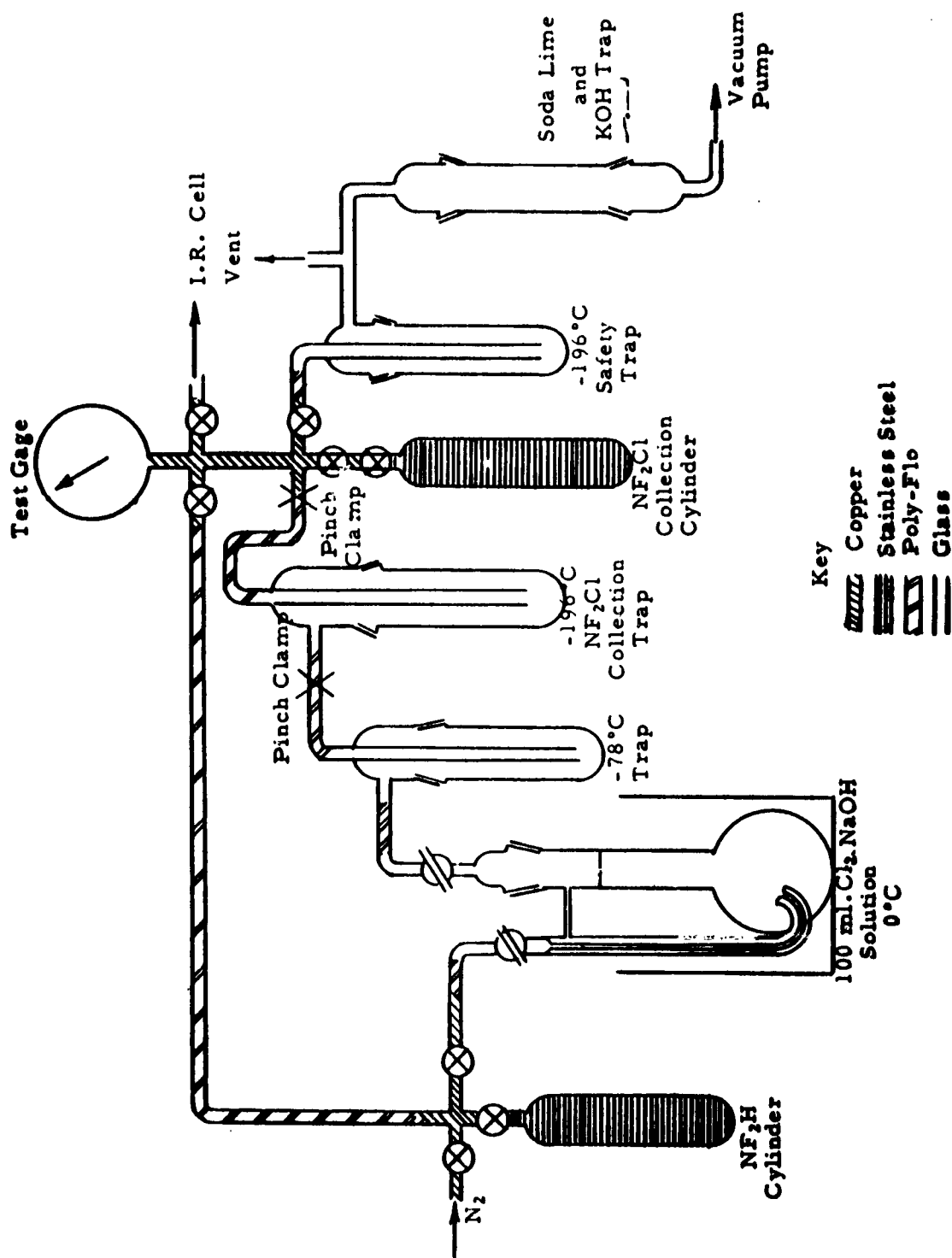
through the capillary tube into the solution, small bubbles are formed. An increase in the NF_2H flow rate produces a head of foam on the solution surface and this serves as a measure of flow rate. The NF_2H is allowed to bubble through the solution for 1-$1/2$ hours. Dry nitrogen then is passed through the solution for another 10-15 minutes. The trap at -196°C. is isolated from the rest of the system and the trap and transfer section of the apparatus evacuated. When the bath is lowered, the light yellow solid found in the trap at -196°C. liquifies quickly to a clear light yellow solution. This liquid then is distilled into a pre-cleaned stainless steel cylinder held at -196°C. For storage the cylinder is placed in a cold box freezer (-10°C). The product shows very little decomposition on standing as long as a week under these conditions.

Results and Discussion: Using the procedure described, NF_2Cl can be prepared in satisfactory yield and high purity. The infrared spectrum of the product is reproduced in Figure 60. The purity of the NF_2Cl is determined by measuring the amount of N_2F_4 present in the NF_2Cl employing previously prepared plots of $\log {}^{I_0}/I$ for pure N_2F_4. The plots for NF_2Cl then were prepared from a product sample containing 5% N_2F_4. The results of the Beer's Law plots at several absorbancies are given in Figures 58 and 59. Mass spectrometry has been found to be unsatisfactory and should not be used for quantitative analysis of NF_2Cl.

3. Synthesis and Some Properties of $FOClO_3$

Fluorine perchlorate was first prepared in 1947 by Cady (54). Little use has been made of it since that time and information concerning its properties and behavior is scarce. There also are reports questioning aspects of the original synthesis (95, 96). In view of its potential as an intermediate in oxidizer syntheses, we investigated its preparation and some of its properties.

Cady, in his original work, first passed fluorine through a packed column containing 72 per cent perchloric acid. He later recommended passing the fluorine over the acid in a platinum boat as being the best procedure for making $FClO_4$. We have found it most convenient to simply pass the fluorine through 70 per cent perchloric acid in a Pyrex glass reactor at 25°C. This method was suitable for laboratory synthesis and more than 40 grams was prepared.

Confirmation of $FOClO_3$ was obtained via molecular weight determination (theo., 118.5; found, 119.8 and 120.4) and elemental and instrumental analyses. Elemental analysis showed
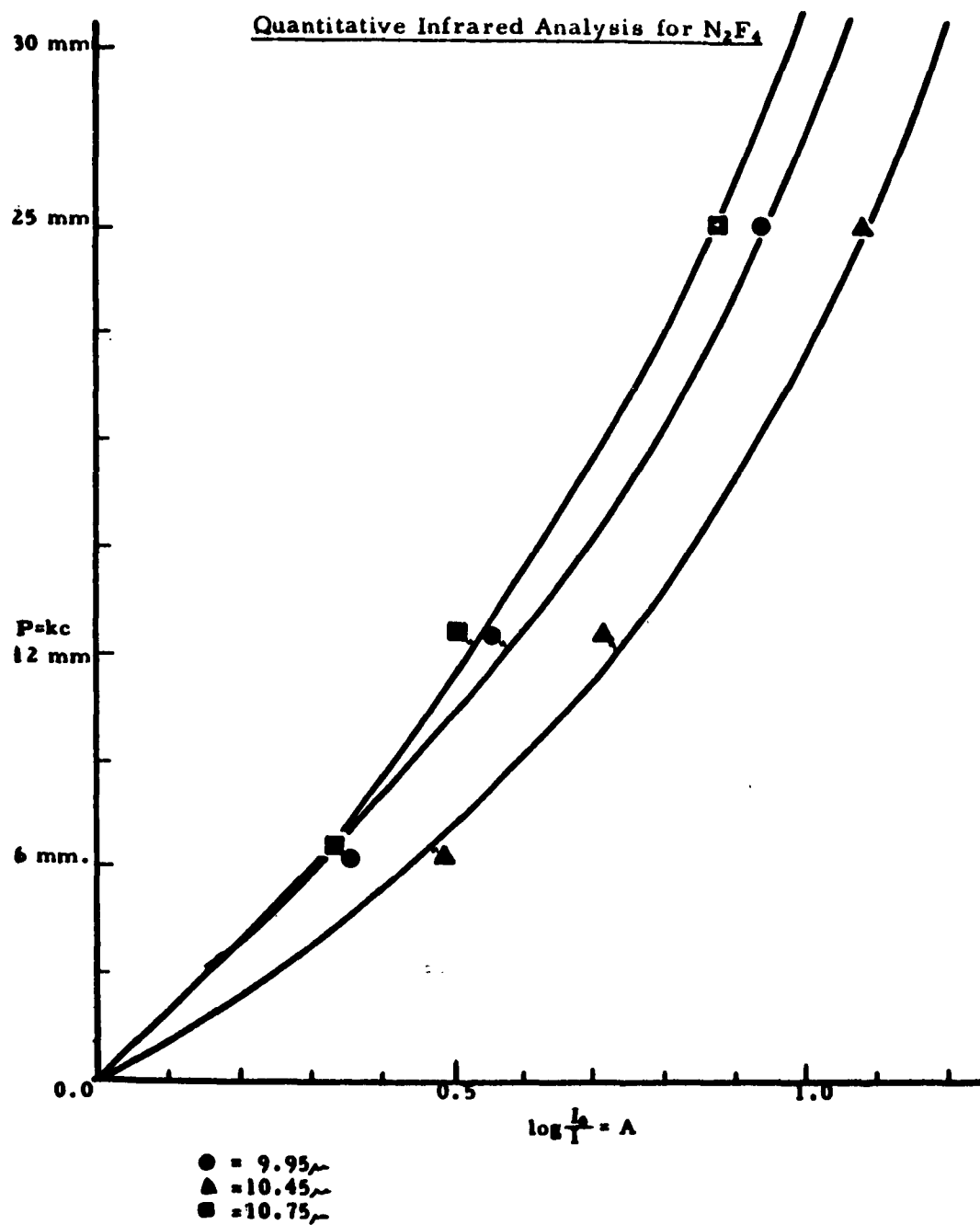
		Found	Theory for $FOClO_3$
Wt. %	F	16.1	16.0
	Cl	27.5	29.9

The infrared spectrum (Figure 62) is that of a sample of vapor exerting 5 mm. of pressure. The cell had an optical path length of 5 cm. and was constructed of Monel with NaCl windows sealed with fluorolube

Figure 58

Quantitative Infrared Analysis for N_2F_4
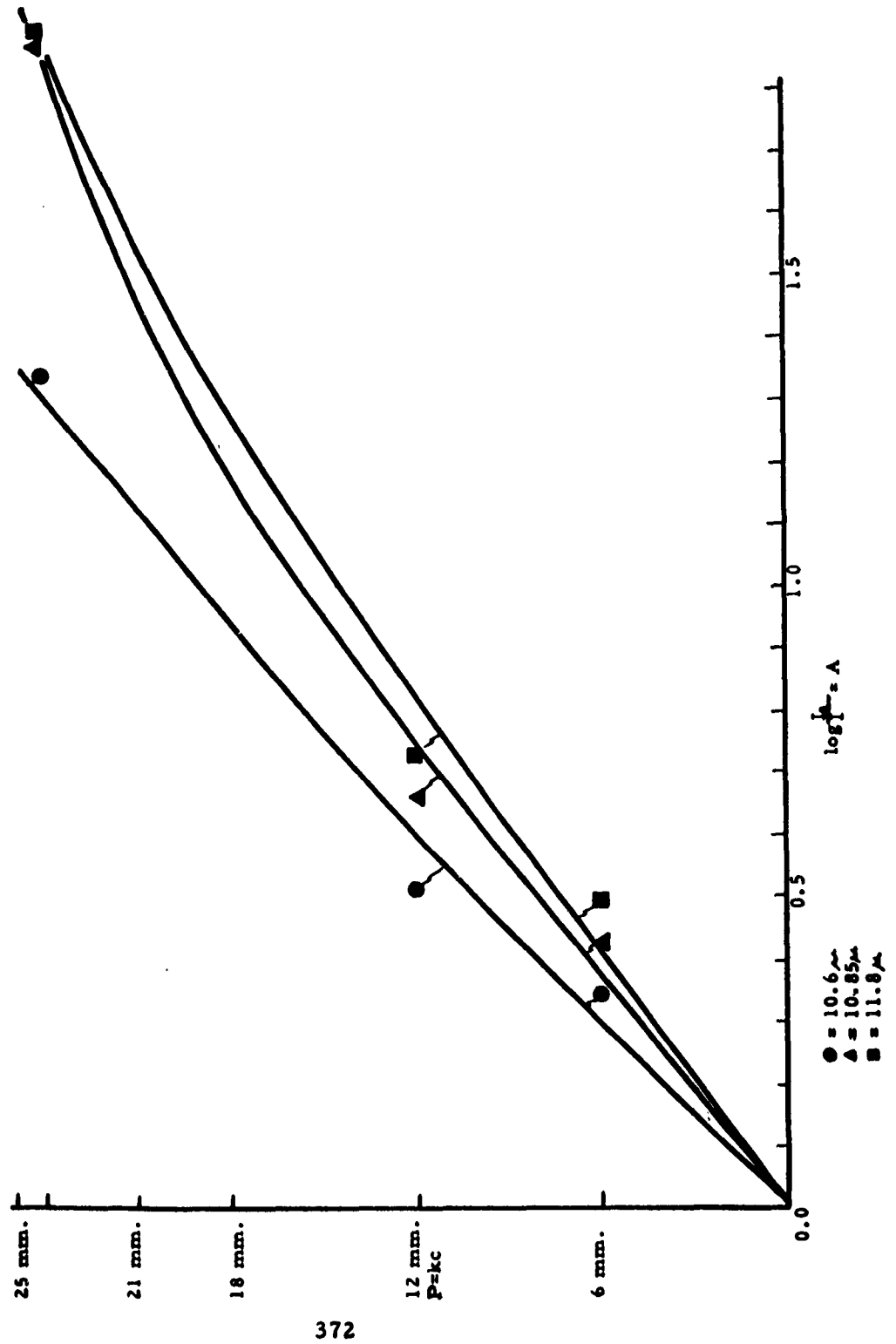
371

Figure 59

Quantitative Infrared Analysis for NF₂Cl

Figure 60

Infrared Spectrum of NF_2Cl
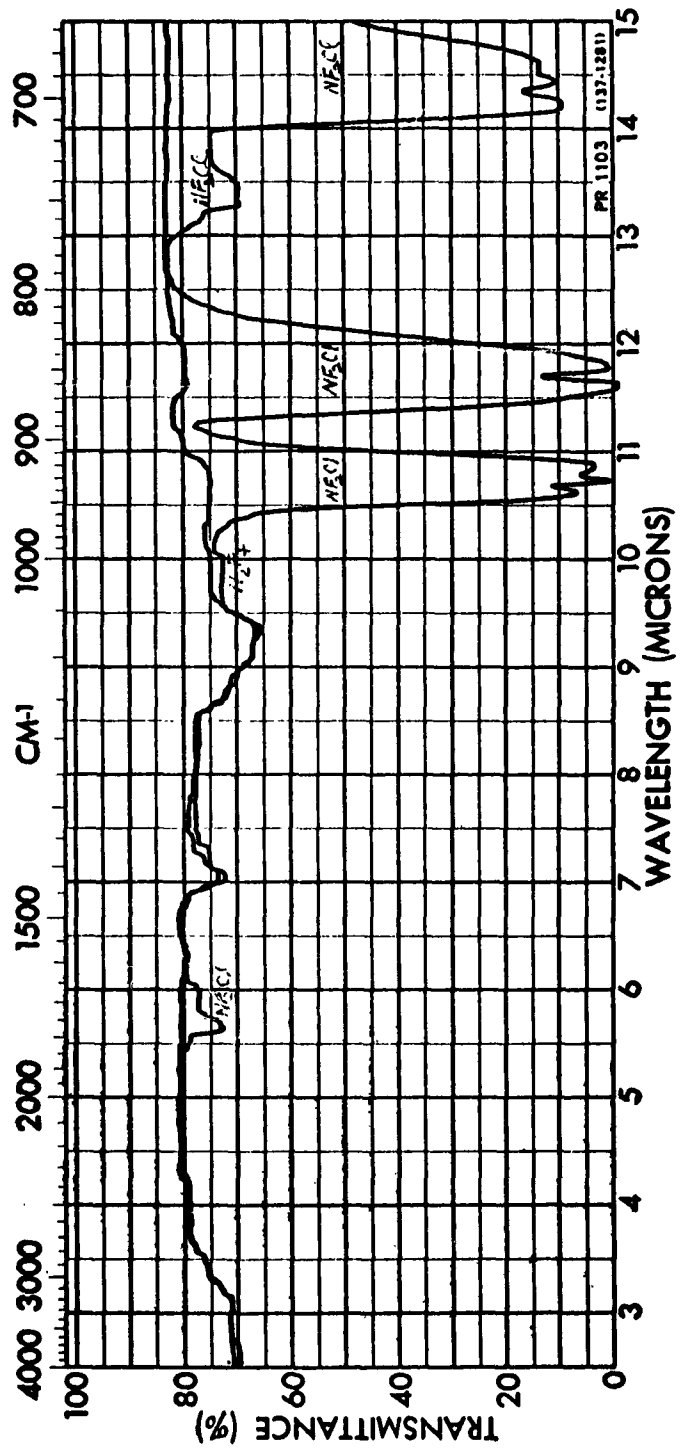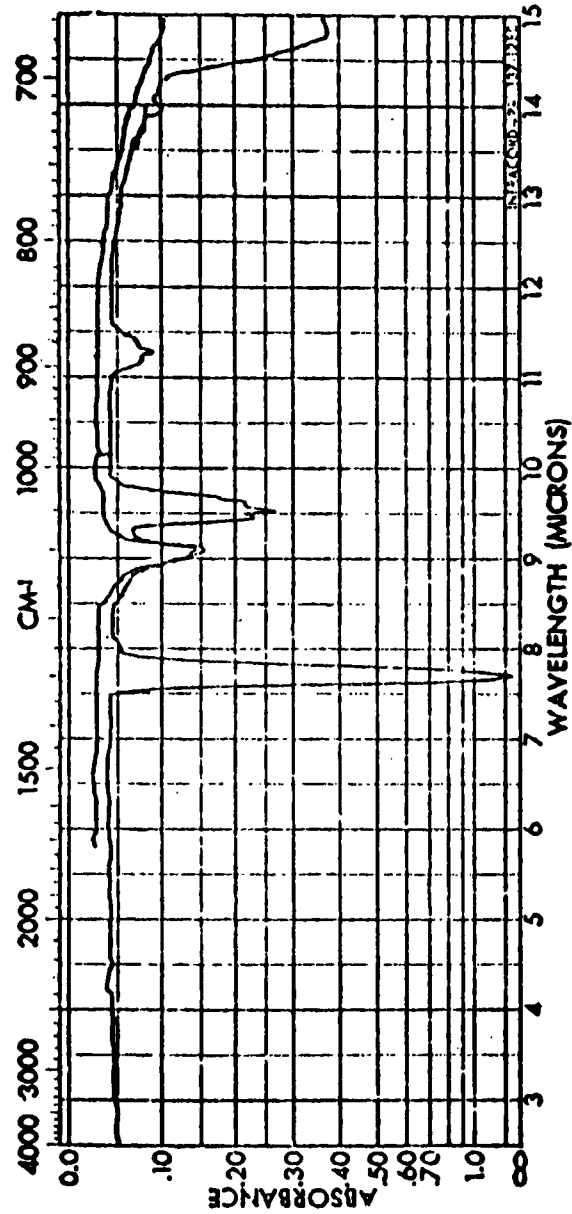
Figure 62

Infrared Absorption Spectrum of Fluorine Perchlorate

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wax. The upper curve is the blank spectrum of the cell after evacuation (the permanent absorption at 9.1μ is due to ClO_4^- produced on the salt windows from a previous sample).

The spectrum exhibits principle absorption band centers at 7.70μ, 9.50μ, 11/29μ and 15.02μ. The latter does not wholly appear on this spectrum, but the extended curve reveals an absorption maximum at 15.15μ similar to that at 14.89μ, with the minimum band center occurring at the reported value. A weak absorption maximum occurs at 13.95μ, which may be a combination of overtone bands of the main component. The scanning of several separately prepared samples has established that the four reported bands occur at constant relative intensities, which lends support to their identification with the same compound. The shoulders at 9.62 and 9.68, however, vary in intensity from sample to sample, and undoubtedly are due to an impurity. On the basis of a reported Raman line at 9.69μ, the shoulders are taken to be due to traces of $HClO_4$.

The two bands in the regions 7.70μ and 9.50μ are characteristic of symmetrical and antisymmetrical stretching vibrations in simple compounds containing the covalently bonded ClO_3 group, such as $HClO_4$, Cl_2O_7 and $FClO_3$. The bands of $FClO_3$ in these regions are, in fact, nearly identical in position to that of the submitted sample However, the band structure of $FClO_3$ at 9.42μ is a triplet (PQR), whereas the sample has a doublet (PR) at 9.50μ. The band at 11.29μ is undoubtedly an O-F stretch. In F_2O, this absorption occurs at 10.77μ and in CF_3OF at 11.36μ. The band at 15.02μ can similarly be assigned to a singly bonded Cl-O stretch. The corresponding absorption in Cl_2O is found at 14.53μ.

The observed infrared spectrum is entirely consistent with the identification of the product as $FOClO_3$. The number, shape and position of the bands are as expected for this compound.

The NMR spectrum of this compound also was recorded and found to consist of a single peak at -225.9 ppm relative to CCl_3F as an internal standard. This is in the region of a typical -OF grouping. This low field resonance position is due to the electronegativity of the perchlorate. In comparing this with perchloryl fluoride and OF_2, it assumes a position of a higher field than either of them.

ClO_3F	-287.1 p.p.m.
OF_2	-250 p.p.m.
$FOClO_3$	-225.9 p.p.m.

These values are all measured from CCl_3F.

The vapor pressure of $FOClO_3$ was measured at -78°C. and -42°C. and found to be 33.0 mm. and 242.4 mm., respectively. This, in conjunction with the reported boiling point of -15.9°C., supplied sufficient data to derive a working curve for the vapor pressure. This was of considerable value in providing a rapid check of purity.

$$\log P = 7.2 - \frac{1,112.06}{t + 273.2}$$

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Figure 63

Vapor Pressure of FOClO$_3$

T °C ⟶

376
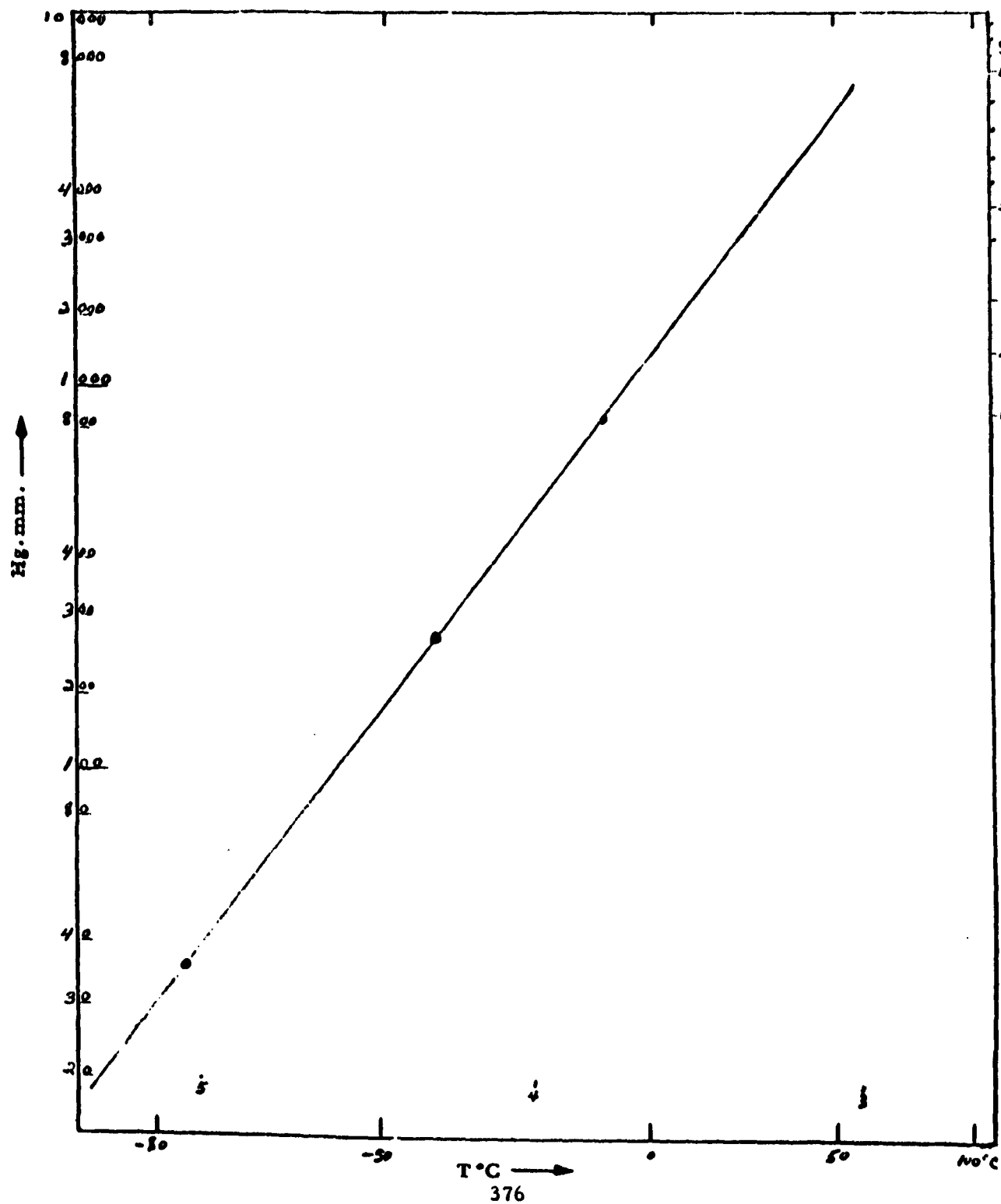
A plot of vapor pressure vs. temperature appears as Figure 63.

Fluorine perchlorate is an extremely reactive substance and in one experiment exploded on contact with water. It can be stored at -78°C. in glass for extended periods of time without decomposition. It also can be stored in steel cylinders, but there appears to be a gradual decomposition at room temperature. In one instance a quantity sufficient to produce three atmospheres of pressure was transferred to a steel cylinder, but detonated in the cylinder when it reached room temperature. It is soluble in carbon tetrachloride and Freon -11($CFCl_3$) which provides a means for performing reactions in solution.

Electronegativity of the Perchlorate Group

As a basis for predicting the course of reactions of N_2F_4 or NF_2H with fluorine perchlorate, the electronegativity of several groups was calculated using the method of Wilmshurst (75) and the following values were obtained:

	X
$-ClO_3$	4.04
$-OF$	3.69
$-ClO_4$	4.62

The ClO_4 group calculation was most open to doubt since the calculation required values for the atomic radii of oxygen and chlorine in ClO_4, information which is not available and had to be approximated. The hydrogen stretching frequency for anhydrous perchloric acid was recently published by Giguere and Savoie (93). Wilmshurst (94) in a later publication suggested that the vibrational frequency for H-X can be used for the group electronegativity calculation of X by employing the following equation:

$$X_x = 1.104 \times 10^{-3} \left(1 + \frac{MH}{MX} \right)^{-1/2} H_x \ (cm^{-1}) - 0.24$$

Using the value of 3560 cm.$^{-1}$ reported by Giguere for the hydrogen stretching frequency of anhydrous perchloric acid vapor, the group electronegativity of ClO_4 is found to be 3.68. This appears to be a more reasonable value than the higher one reported earlier and suggests that in the molecule $FOClO_3$ cleavage of the bonds may produce simultaneously F and OF radical formation.

$$
F-O-ClO_3
\begin{cases}
\nearrow & F + ClO_4 \\
& 4.0 \quad\quad 3.7 \\
& \text{---------------} \\
& 4.0 \quad\quad 3.7 \\
\searrow & ClO_3 + OF
\end{cases}
\quad \text{electronegativities}
$$

The electronegativity calculations are also in agreement with NMR spectra. Although the relationship between chemical shift and

electronegativity has had only limited application and is very complex, there is some correlation when comparisons are made with similar compounds. The NMR fluorine peaks of perchloryl fluoride, oxygen difluoride and fluorine perchlorate are reproduced here, relative to CCl_3F as an internal standard.

$F-OClO_3$	-225.9	p. p. m.
$FO-F$	-250	p. p. m.
$F-ClO_3$	-278	p. p. m.

Since the fluorine peak in fluorine perchlorate assumes a position of higher field than the others, it suggests a higher electron density on the fluorine and therefore a lower electron density for ClO_4.
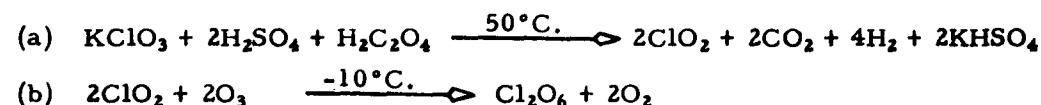
4. Synthesis of Cl_2O_6

A laboratory method for the synthesis of dichlorine hexoxide is described by Bodc and Klesper (29). At 40-60°C. fluorine gas reacts with dry $KClO_3$ to form KF and Cl_2O_6.

$$F_{2(g)} + 2KClO_{3(s)} \xrightarrow{50°C.} Cl_2O_6 + 2KF$$
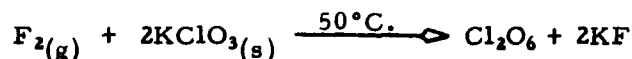
The surprising aspect of this reaction is that when lower temperatures are employed the reaction becomes an excellent preparative method for $FClO_3$.

Our attempts to prepare Cl_2O_6 by this method were unsuccessful in spite of repeated efforts and a variety of conditions. Generally, we obtained $FClO_3$ by this reaction. It is possible that some moisture is necessary to promote the desired reaction, but this was not confirmed in our work.

Due to the difficulty experienced in duplicating the reaction of $KClO_3$ with fluorine, attention was directed to an alternate method for the preparation of dichlorine hexoxide, based on the following reactions:

(a) $KClO_3 + 2H_2SO_4 + H_2C_2O_4 \xrightarrow{50°C.} 2ClO_2 + 2CO_2 + 4H_2 + 2KHSO_4$

(b) $2ClO_2 + 2O_3 \xrightarrow{-10°C.} Cl_2O_6 + 2O_2$

Materials

KClO_3. Allied Chemical and Dye Corp. , General Chemical Div. , Reagent Grade.

$H_2C_2O_4 \cdot 2H_2O$. Mallinckrodt Chemical Co. , Reagent Grade.

H_2SO_4. Mallinckrodt Chemical Company, Reagent Grade.

O_2. The Linde Company

Apparatus

The apparatus is described in Figure 23.

Procedure

In a typical preparation, 4 grams of $KClO_3$ and 4 grams of $H_2C_2O_4 \cdot 2H_2O$ were placed in the Pyrex reactor R_1 and cooled to $0°C$. Concentrated sulfuric acid (2. 2 ml.) was dissolved in 16 ml. of distilled water, the solution placed in the addition funnel A and a $-10°C$. bath placed around reactor R_2.

Oxygen was then passed into the Ozonator at the rate of 0.15 CFM at 8 p. s. i. g. and the ozonator was started. The sulfuric acid solution was slowly added to reactor R_1 with stirring. The solution in R_1 was then warmed to $70°C$. and dry nitrogen gas used to dilute the ClO_2 and to force it into reactor R_2 where a reaction occurred between the ozone and chlorine dioxide. After the evolution of ClO_2 in R_1 subsided, (about two hours) the residual ClO_2 in the system was flushed with nitrogen and vented. The Cl_2O_6 was distilled under vacuum from reactor R_2 to the Teflon coil R_3 at $-78°C$. The Cl_2O_6 in R_3 was purified by passing dry nitrogen gas through the Cl_2O_6, about 1-1.5 grams was stored at $-78°C$. in the Teflon coil until used.

Approximately 75 grams of Cl_2O_6 was prepared by this method and the purified Cl_2O_6, a blood red, viscous, liquid showed a melting point slightly lower than the published value, 3.5°C. An infrared analysis of the Cl_2O_6, dissolved in CCl_4, showed Cl-O bands in the 9-10 micron region; however, the masking of some bands by carbon tetrachloride is probable.

Attempts to obtain an infrared spectrum of liquid Cl_2O_6 at 25°C. using sodium chloride windows were unsuccessful due to attack on the cell windows. Similarily, attempts to obtain an infrared of the viscous liquid between Irtran plates were unsuccessful due to severe etching of the Irtran and the hygroscopic nature of the Cl_2O_6.

The Cl_2O_6 was stored in Teflon at $-78°C$. and shielded from light for several days with no observed pressure increase due to decomposition. During the course of handling purified Cl_2O_6 at 25°C. there were no incidents of explosion due to shock or rapid heating to 50°C., although at 50°C. some decomposition occurred.

5. Preparation of N_2F_4

When laboratory quantities were needed for exploratory experiments, and the N_2F_4 was not available commercially, an apparatus was constructed for the preparation of this intermediate by the following reaction:

$$2NF_3 + Cu \xrightarrow{\quad 500°C. \quad} N_2F_4 + CuF_2$$
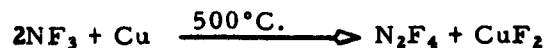
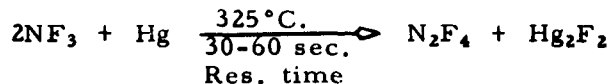The apparatus is described in Figure 64 and the results of a series of experiments are shown in Table 89.

The yields of N_2F_4 and conversion of NF_3 were generally unpredictable. The reaction apparently is influenced to a large degree by such variables as surface area of the copper packing, the nature of the diluent gas, flow rates, temperature, and activity of metal surfaces.

In the initial experiments, with fresh copper packing, the products consisted of nitrogen oxides and nitrogen. After the oxides were depleted, yields of N_2F_4 generally increased. However, complete decomposition occurred at times, possibly due to localized hot spots in the copper bed, possibly by the following reactions:

$$2NF_3 + 3\,Cu \longrightarrow 3\,CuF_2 + N_2$$

$$N_2F_4 + 2\,Cu \longrightarrow 2\,CuF_2 + N_2$$

In view of the erratic performance of this system a more efficient method was sought. The Stauffer Chemical Co. preparation by the reaction of NF_3 with carbon was considered, but in this method the recovery of both N_2F_4 and NF_3 is difficult due to the close boiling points of the by-products CF_4 and C_2F_6.

Dr. R. D. Dresdner, University of Florida (97) described a method for the synthesis of N_2F_4 based on the reaction of NF_3 with mercury:

$$2NF_3 + Hg \xrightarrow[\substack{30\text{-}60 \text{ sec.} \\ Res. \text{ time}}]{325\,°C.} N_2F_4 + Hg_2F_2$$

The apparatus is described in Figure 65. This method was more attractive for laboratory preparations because there are no volatile by-products and the yields and conversions are more reproducible than those obtained by the copper method.

The results of several typical preparations are listed in Table 90. Generally the yields of N_2F_4 varied between 30 and 60%. In experiments 1848D-37 and 39, the yields were neglibible but the mercury used in these experiments was impure and a viscous amalgam formed in the reactor. This method of preparation of laboratory quantities was satisfactory and the N_2F_4 was of high purity as determined by infrared analysis.

Figure 64

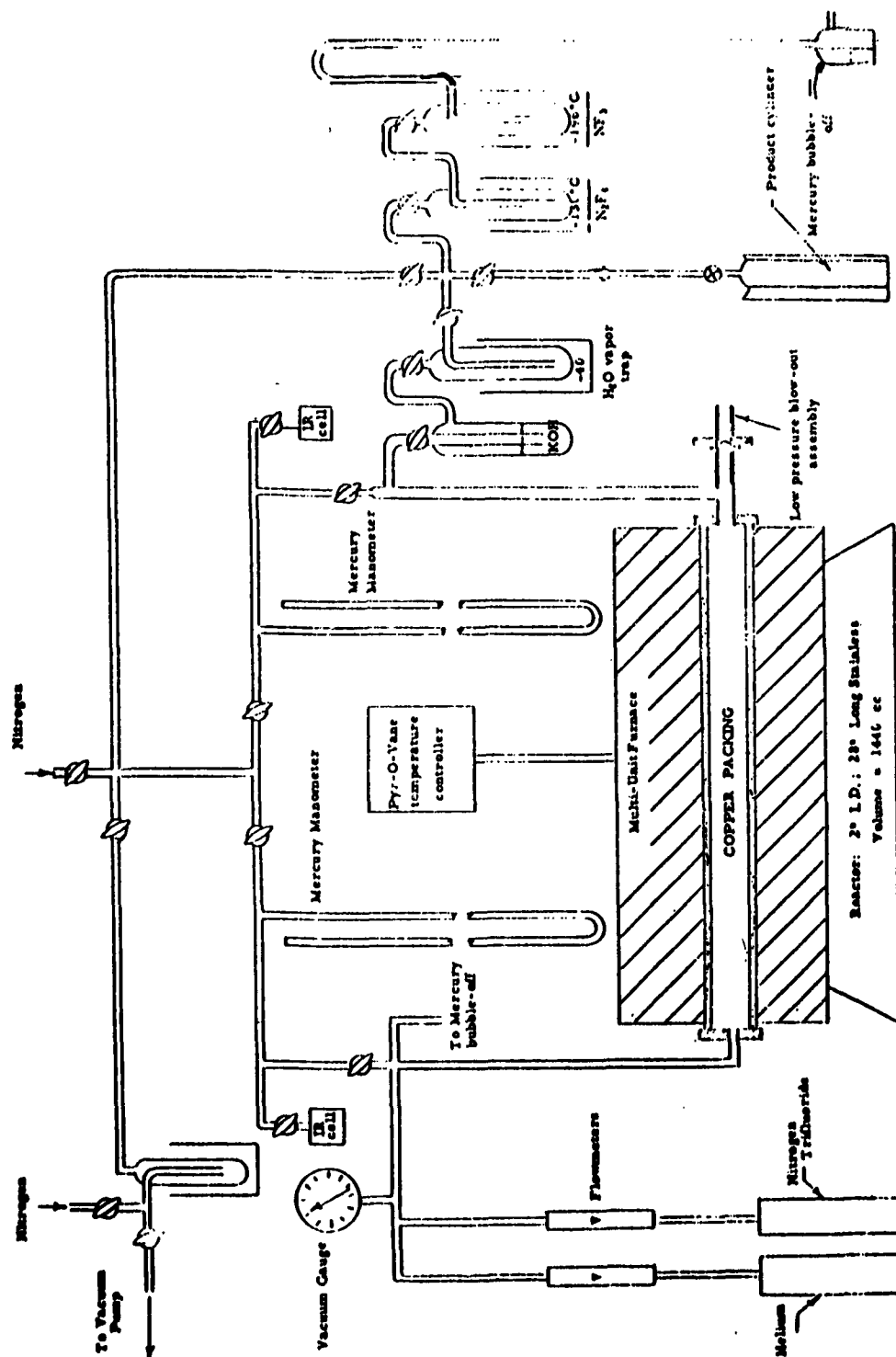Apparatus for the Preparation of N_2F_4

Table 89

Synthesis of Tetrafluorohydrazine (Cooper Reactor)

Experiment Number	Reactor		Reac-tion Time (min.)	Resi-dence Time (min.)	NF₃ Addition ml./min.	He Addition ml./min.	Added g.	NF₃ Re-covered g.	Con-verted %	N₂F₄	
	T °C	Pressure (mm. Hg)								Re-covered g.	Corrected Yield %
1848D-13	528	780	240	7.2	55	10	42	15	64.3	4	20.2
16	526	780	270	7.0	57	10	49	15	69.3	1	4.0
19	525	783	210	6.9	60	10	40	17	57.5	2	11.9
1724D-65	502	780	280	8.5	47	10	42	5	88.1	2	7.4
68	500	785	300	8.2	49	10	47	29	38.2	3	22.8
73	500	750	300	7.8	52	10	49	17	65.3	1	4.3
76	502	780	270	7.2	57	10	49	35	28.6	4	39.0
79	503	775	200	7.2	57	10	36	23	36.1	2	21.0
82	504	780	240	7.0	59	10	45	30	33.3	2	18.□
85	505	780	285	8.3	48	10	43	33	23.3	7	45.6
88	515	780	270	6.8	60	10	51	27	47.1	8	45.5
92	507	770	270	12.7	28	10	24	8	66.7	3	25.6
95	503	775	270	8.1	50	10	43	24	44.2	3	13.9
98	501	780	270	8.0	51	10	44	29	34.1	<1	
101	504	780	240	8.1	50	10	38	28	26.3	<1	
1848D-8	504	780	170	7.6	54	10	29	16	44.8	<1	

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Figure 65

Apparatus for the Preparation of Tetrafluorohydrazine

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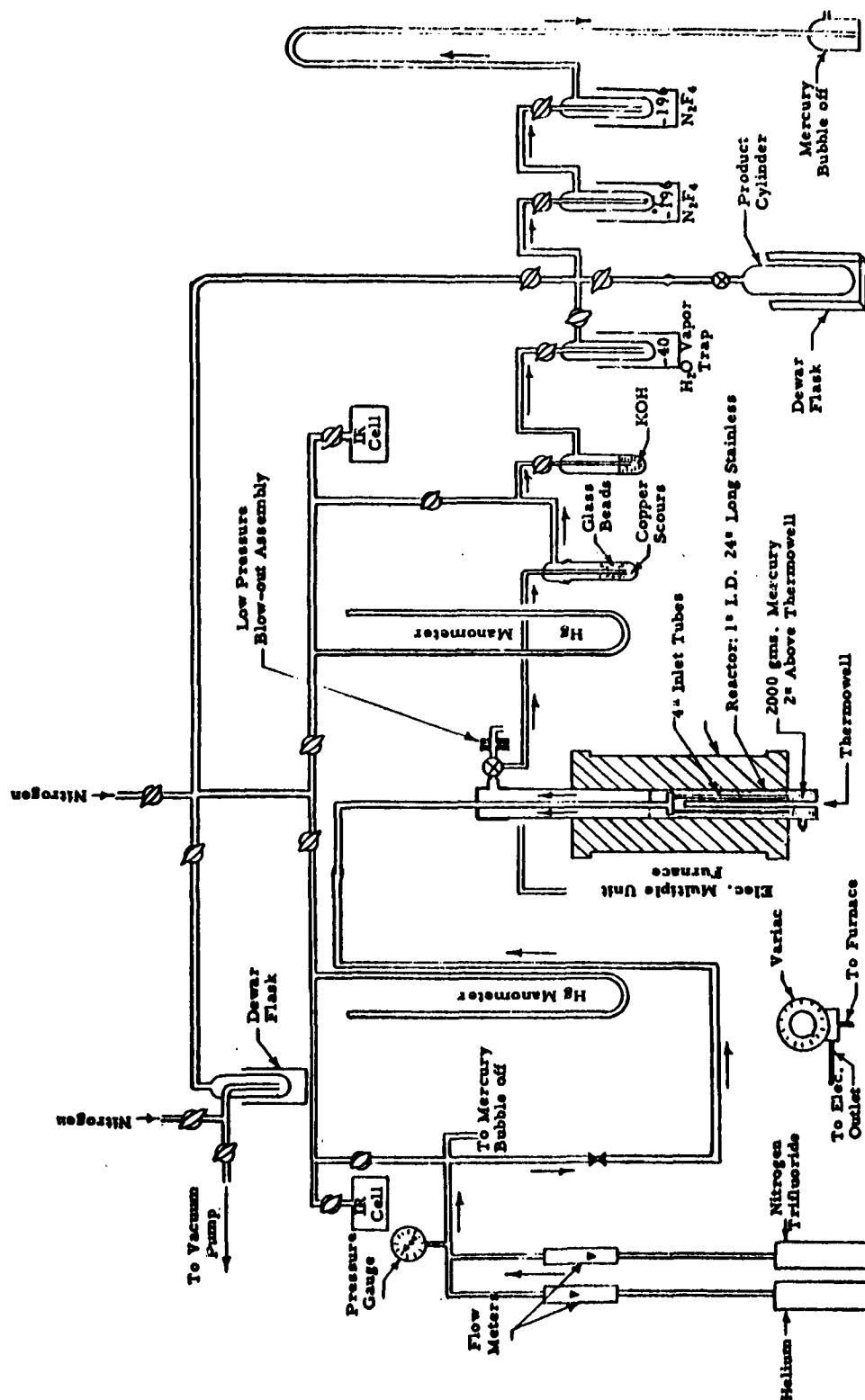
Table 90

Synthesis of Tetrafluorohydrazine (Mercury Reactor)

Experiment Number	Reactor		Reac- tion Time (min.)	Resi- dence Time (min.)	NF$_3$ Addition ml./min.	He Addition ml./min.	Added g.	NF$_3$		N$_2$F$_4$	
	T °C	Pressure p.s.i.						Re- covered g.	Con- verted %	Re- cov- ered g.	Corrected Yield %
1848D-30	321	8	50	1.1	69	6	11	2	81.8	2	30.3
33	334	3	80	0.7	114	10	29	18	47.9	4	49.7
35	340	8.5	180	0.7	88	27	50	32	29.9	4	30.3
37	326	5	140	0.7	90	22	40	18	55.0	0	0
39	326	19	205	0.8	88	10	57	50	14.0	0	0
49	325	2.6	160	0.8	93	10	47	38	23.7	4	60.7

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